AGGRADING LATERITIC SOILS (ULTISOL) USING BIOCHAR

by

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(2015-21-003)

THESIS

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DECLARATION

I, hereby declare that this thesis entitled **"Aggrading lateritic soils (Ultisol) using biochar"** is a bona-fide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other University or Society.

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CERTIFICATE

Certified that this thesis, entitled **"Aggrading lateritic soils (Ultisol) using biochar"** is a record of research work done independently by **Mr. R. Rajakumar (2015-21-003)** under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to him.

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(R. Rajakumar)

Symbols / Notations and Abbreviations

µg TPF g^{-1} soil 24hr^{-1} - Microgram TPF per gram soil per 24 hour
AAN - Amino acid nitrogen
BET - Brunauer Emmett Teller
cmol (+) kg^{-1} - Centimole proton per kilogram
CD - Critical difference
CRD - Completely Randomized Design
dS m^{-1} - Deci Siemen per meter
DAS - Days after sowing
DMP - Dry matter production
DHY - Dehydrogenase activity
EC - Electrical conductivity
ESR - Electron spin resonance
et al. - Co-workers
Fig. - Figure
FT-IR - Fourier-transform infrared spectroscopy
GDP - Gross domestic product
GHG - Greenhouse gas
GWP - Global warming potential
HWSC - Hot water soluble carbon
kPa - Kilo Pascal
LFC - Light fraction carbon
MPa - Mega Pascal
meq 100g^{-1} - Milli equivalents per 100 gram
Mg m^{-3} - Mega gram per cubic meter
mmol g^{-1} - Milli moles per gram
MSL - Mean sea level
MAI - Months after incubation
MRT - Mean residence time
MWHC - Maximum water holding capacity
MWD - Mean weight diameter

MBC - Microbial biomass carbon

NMR - Nuclear magnetic resonance

NO_3-N - Nitrate nitrogen

NH_4-N - Ammoniacal nitrogen

OPSTAT - Online agriculture data analysis tool

Pg - Petagram

PGPR - Plant growth promoting rhizobacteria

POP - Package of practices

POM - Particulate organic matter

POXC - Permanganate oxidizable carbon

Py-GCMS - Pyrolysis-gas chromatography-mass spectrometry

RDF - Recommended dose of fertilizers

RBD - Randomized block design

SEM - Scanning electron microscope

SOC - Soil organic carbon

SOM - Soil organic matter

SPSS - Statistical package for social sciences

THyN - Total hydrolysable nitrogen

TPF - Tri Phenyl formazan

TEM - Transmission electron microscope

TGA-MS - Thermogravimetric analysis-Mass spectrometry

USDA - United States Department of Agriculture

WSC - Water soluble carbon

WUE - Water use efficiency

WASP - Web Agri Stat Package

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Introduction

1. INTRODUCTION

Agriculture holds a key position in Indian economy constituting 17.32 per cent of GDP with 47 per cent of its working population employed in agriculture sector. This sector confronts different issues like shrinking of average land-holding size, use of arable land for other purposes and land degradation. The use and management of soil and water by humanity have shaped the growth decline and rejuvenation of human civilization that are assisted by agriculture. Ideal soils for agriculture are balanced in contribution from mineral components, soil organic matter, air and water. Managing soil health can be a tool to enhance productivity of the existing arable land to produce the food required for the ever increasing population.

Kerala is unique as far as its soils are concerned which includes red loam, laterite soil, coastal alluvium, riverine alluvium, Onattukara alluvium, brown hydromorphic, saline hydromorphic, Kuttanad alluvium, black soil and forest loam. The state has been described in the earth science literature as the 'type locality of laterite', a name first pointed out by Francis Buchanan in 1800 at Angadipuram of Malapppuram district of the state. The term laterite owes its origin to the Latin word 'Later' meaning 'Brick'. These soils on drying form hard impenetrable and often irreversible pans which makes the naming appropriate. Laterite and lateritic soil are formed by intensive and prolonged weathering of the underlying parent rock. Classified under the order Ultisols, these acidic soils cover nearly 65 per cent of the total geographical area occupying midlands and mid upland regions of Kerala (KAU, 1989). The tropical climate prevailing in the region characterized by heavy rainfall and high temperature, leading to alternate wet and dry seasons favour the process of laterization. The soils are generally acidic (with Fe, Al and Mn in toxic levels), low in CEC, low to moderate in base saturation, dominant in kaolinite clay, rich in sesquioxides, poor in inherent fertility and high in P fixation. The compact B horizon that inhibits root penetration, reduced soil volume, low level of organic matter, decreased moisture retention *etc.* are the major constraints to crop production which can be overcome through the practice of green manuring, legume based crop rotation, regular application of manures and fertilizers and liming materials.

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Plantation crops, food and fruit crops, spices, beverages and stimulants and vegetables are normally grown successfully in laterite soils.

As far as laterite soils are concerned, the continuous application of organic manures and amendments is highly essential because of soil compaction and high rate of mineralization associated with tropical situation. It is in this context that 'biochar' which is an amendment highly resistant to decomposition serves as a viable proposition.

Biochar (Agrichar or black carbon) can be made from a variety of raw materials that are lignocellulosic or non-lignocellulosic. Usually the lignocellulosic biomass are abundant bio-resource including agro-industrial residues, forest industrial residues, energy crops, municipal solid waste and others. Kerala, the land of coconut with an area of 7.70 lakh ha under this crop, producing 7448.65 million nuts per year has plenty of biomass in terms of coconut shell and husk that can be used for biochar production. A single coconut fruit has nearly 40-50 per cent husk and 15 per cent shell. The shell which is the strongest part of the fruit is of immense use in handicraft industry to produce many novel products besides yielding shell based charcoal, activated carbon, and powder. The coconut husk is the source of natural fibre, 'coir' from which an array of products are manufactured. Another common use of husk is for conserving moisture in agricultural lands during summer months and as fuel. Even after all these uses to which the coconut shell and husk are put into, plenty of it accumulates that are disposed either by burial or burning.

Often the open burning of any biomass leads to the emission of gases like CO_2, CH_4, CO, N_2O, NH_3, SO_2, volatile organic compounds and particulate matter into the atmosphere, contributing to environmental changes and global warming. Furthermore, 'ash' the resultant product of complete burning contains only very few nutrient elements like, P, K, Ca, Mg and some micronutrients. For this reason, burning cannot be considered as a viable method for managing any bio waste. However, these can effectively be recycled by transforming into 'biochar', a relatively a new green technology management tool, through the process of pyrolysis wherein the organic material is thermally decomposed under limited supply of O_2 and at relatively low temperature. This methodology is infact the modern version of

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an ancient pre-Columbian technology invented by native Amazonian people to enhance soil fertility.

Biochar is defined as a carbon rich product derived from the slow pyrolysis (heating in the absence of oxygen) of organic material at relatively low temperatures (<700°C) (Lehmann, 2007). It possess the ability to store carbon for longer periods of time as it is more stable in soil (may be 100-1000 years) chemically and biologically than the source material. Production of biochar and its storage in soils has been suggested as one of the possible means of reducing the atmospheric CO_2 concentration. Biochar's climate mitigation potential stems primarily from its highly recalcitrant nature which reduces the rate at which photosynthetically fixed C is returned to the atmosphere. Considering the possible strategies to remove CO_2 from the atmosphere, biochar is notable, if not unique, in this regard for sequestering carbon in soil thus mitigating climate change effects and global warming.

Amelioration of degraded soil and reduction of soil acidity brought about by biochar addition are made possible by the chemically reactive groups (such as carboxyl, hydroxyls and ketones) which help to adsorb toxic substances like Al and Mn from acid soils (Abewa *et al.*, 2014; Masud *et al.*, 2014; Lin *et al.*, 2018). As against the uncharred raw material, biochar becomes biochemically recalcitrant because of the dominance of aromatic carbon. The increased surface area offers higher potential to hold water and nutrients leading to increased crop growth and production. Improvement in soil pH, increase in CEC (Cheng *et al.*, 2006) increased biological nitrogen fixation, reduced leaching loss of nutrients, especially nitrogen into the ground water (Ding *et al.*, 2010) and that of phosphorus into the surface water, creation of favourable environment for microbial activity and decreased degradation of the soil stand out as the positive effects of biochar application. The carbon contained in biochar is by and large stable and aromatic which makes it unavailable to the microbes. But it is revealed that the metabolisable fraction of carbon present even in minute quantities would alter soil nitrogen transformation process which necessitates studying the C and N dynamics in soils added with biochar. Crop yield improvement on applying biochar as an amendment has been reported through enhancing water holding capacity, CEC, higher absorption of plant nutrients and creation of a favourable environment for soil microorganisms (Dugan *et al*., 2010; Islami *et al*., 2013; Carvalho *et al*., 2014; Akshatha, 2015; Dainy, 2015).

In order to unwind the probable effect of the amendment biochar on yield promotion, Chinese potato [*Solenostemon rotundifolius* (Poir.)] and vegetable cowpea [*Vigna Unguiculata* (L.) Walp] were utilized as test crops in the present study. Chinese potato or coleus is a tropical tuber crop grown for its edible tubers which is used as a vegetable. Due to the peculiar aroma, high starch and content of minerals and vitamins it fetches a good price in the market. Another vegetable of prominence and preference in Kerala's context is the vegetable cowpea which can be cultivated throughout the year.

Accounting the properties of laterite soils and the positive traits of biochar, the present investigation titled "Aggrading lateritic soils (Ultisol) using biochar" was undertaken with the following objectives:

- To produce biochar from coconut based material and characterize it for physical and chemical properties
- To study the dynamics of carbon and nitrogen in lateritic soil applied with different levels of biochar with time and
- To study the direct and residual effect of biochar on growth, yield and quality of Chinese potato and cowpea, respectively and on soil properties

Review of Literature

2. REVIEW OF LITERATURE

The present investigation entitled "Aggrading lateritic soils (Ultisol) using biochar" was undertaken at the College of Horticulture, Vellanikkara and Agricultural Research Station, Mannuthy during 2016-2018. Literature pertaining to the production of biochar and its characterization, dynamics of C and N under biochar application, direct and residual effect of biochar on crops and its effect on soil properties are critically reviewed in this chapter.

Biochar

Biochar, a carbon rich material is derived by heating organic biomass (250-700°C) with limited supply of O_2. The term biochar is reserved for the plant biomass derived materials contained within the black C continuum (Lehmann *et al.*, 2006). By being chemically and biologically more stable (Lehmann and Joseph, 2009), it differs from the original plant materials thus contributing to long term removal of CO_2 from atmosphere. Biochar differs from charcoal, activated carbon and other black carbon materials. However, the differences are comparatively subtle, since all products are obtained from the burning of C rich substance. Upon heating, the polymeric building blocks present in the plant residues go through cross linking, depolymerization and fragmentation, getting itself converted to 2D structure of fused rings. This further appears as stacked crystalline graphite sheets and randomly ordered amorphous aromatic structures. Within the aromatic rings are incorporated the H, O, N, P and S as heteroatoms contributing to the highly heterogeneous surface chemistry and reactivity of biochar.

History of Biochar

In the recent years, there is much interest in using biochar as soil amendment to improve and maintain soil fertility and to increase C sequestration. The capacity to sequester C in the soil can be attributed to the relative stable nature and the long MRT of biochar in soil adding on to its relevance in climate change mitigation. Though it is difficult to estimate how long newly added biochar will remain in the soil, few researchers are of the opinion that it could be upto 5000 years even.

The historical use of biochar dates back at least 2500 years in the Amazon basin, which were created by ancient indigenous civilization leaving the imprints of extensive biochar use in the unusually fertile soils designated as terra preta and terra mulata. Since large amount of biochar incorporated into its soils, soils of this region remained highly fertile despite leaching for centuries. In part of Asia, also notably Japan and Korea, biochar use in agriculture has a long history (O'Neill *et al.*, 2009).

Biochar production

Thermochemical decomposition of condensed substances by heating under O_2 controlled condition yields the product 'biochar'. Different thermochemical conversion processes used in the production of biochar are pyrolysis, gasification and hydrothermal conversion. In pyrolysis, series of by-products *viz.* biochar, bio oils and syngas (H, CO and CO_2) are derived, whereas, in gasification biochar alone is obtained as by-product.

Number of studies states that the biochar yield is highly dependent on the pyrolysis conditions such as temperature, heating rate and residence time (Uzun *et al.,* 2006; Tsai *et al.,* 2007) and is also greatly influenced by physical, chemical and biological properties of the raw materials used (Tanaka, 1963; Knoepp *et al.,* 2005; Lehmann, 2007; Chan and Xu, 2009; Basta *et al.*, 2011; Conz *et al.*, 2017).

Jindo *et al.* (2014) produced and characterized biochar from different feedstock at varied temperatures ranging from 400-800°C and found that in all the feedstock, biochar yield was inversely related to temperature. The study further revealed that, pyrolysis at low temperature produced high biochar yields, whereas high temperature led to biochar with high C content, surface area, and adsorption characteristics. High recalcitrant nature was observed in biochar produced at 600°C, whereas, that obtained at 400°C retained labile compounds. Similar biochar yields were also reported by Gai *et al.* (2014) for other agricultural by-products such as corn straw (24-35 %), peanut shell (25-36 %) and wheat straw (22-32 %), wherein the biochar yield reduced with increase in temperature from 400 to 700°C.

Among the properties of raw materials, the amount of cellulose, lignin, lignocellulose and hemicellulose have a relevance on the chemical and structural composition of biochar. Winsley (2007) reported that, wood biomass resulted in coarse and resistant biochar with nearly 80 per cent C content, and ascribed it to the stiff ligninolytic nature of the raw material that got retained even in the biochar. Similarly, variation in pH of biochar as influenced by the feedstock was recorded by Yuan and Xu (2011) and Yuan *et al.* (2011). At the identical pyrolysis temperature of 300°C, biochar produced from soybean, peanut and corn straw were all alkaline, whereas the canola, wheat straw and groundnut hull biochar were of acidic in nature.

Raveendran *et al.* (1995) and Nik-Azar *et al.* (1997) reported that greater the concentration of lignin, more was the recovery during pyrolysis. This was further confirmed from the study of Mandal *et al.* (2013). Biochar recovery per cent was more for lignin rich pine wood (34.28 %), followed by 27.72 and 18.34 per cent for Lantana and Chromolaena respectively, which contained comparatively lesser lignin.

The effect of different kilns on the properties of resultant biochar was studied by Pandit *et al.* (2017). Irrespective of kiln types, the biochar produced had uniform pH (9.1), CEC (133 cmol kg^{-1}), organic carbon (73.9 %) and surface area, which helped them to deduce that the properties of biochar was similar for all kilns tried.

Sun *et al.* (2017) produced biochar using different pyrolysis temperature, residence time and concluded that at low pyrolysis temperature (300°C) increasing residence time would result in a gradual reduction in recovery of biochar and a cumulative increase in the pH. However, at high pyrolysis temperature (600°C) increasing residence time had only little effect on the pH or recovery per cent.

Yang *et al.* (2015) conducted a study to assess the effect of climatic conditions prevailing in the feedstock grown area on biochar properties. The study revealed that the nutrient content increased in semiarid and arid regions in comparison to humid regions, whereas, the ash content, total C, CEC, pH, surface acidity, surface basicity showed no correlation with the climate.

On considering the functional groups, more numbers of C in poly-condensed aromatic structures were identified by pyrolyzing organic feedstocks at high temperatures (400-700°C) (Baldock and Smernik, 2002; Glaser *et al.*, 2002; Hamer *et al.*, 2004; Hammes *et al.*, 2006). However, due to dehydration and decarboxylation the number of ion exchange functional groups gets lowered, thus limiting its potential usefulness in soil nutrient retention (Baldock and Smernik, 2002; Glaser *et al.*, 2002). On the other hand, biochars produced at lower temperatures (250-400°C) contained more C-H and C=O functional groups that could serve as nutrient exchange sites after oxidation (Glaser *et al.*, 2002). In addition, low temperature biochars were more diversified and organic in nature, with aliphatic and cellulose type structures (Alexander, 1977).

Characterization of biochar

Depending on the source of biomass, the temperature at which it is heated and the extent to which produced volatiles are separated from the biochar, the properties of biochar vary substantially. Depending on the biochar properties, its effect in soil may differ. This warrants detailed characterization of biochar for their field application to sequester C and upgrade soil fertility.

Biochars produced at high temperature (<550°C), with high ash content, have intricate surface and internal properties that result in complex interactions with the soil components. Regarding the low temperature biochars, they possess primarily amorphous C structure with lower aromaticity (Amonette and Joseph, 2009).

The structure of biochar can be characterized spectroscopically (NMR, ESR, Raman Spectroscopy), chemical/thermal analysis (TGA-MS, Py-GCMS) or microscopically (SEM, TEM). Often, SEM is used to describe the physical structure of biochar and the architecture of cellulosic plant material. As evidenced by SEM image, the final product biochar retains the cell wall structure of the plant biomass (Yu *et al.*, 2006).

Yuan *et al.* (2011) examined the structural characters of biochar using X-ray diffraction spectrum and reported that carbonates were the major alkaline components in the biochars produced at the high temperature (500-700°C). Further the FT-IR data and zeta potentials designated that the COOH and OH functional groups present in the biochars contributed appreciably to the alkalinity of the biochars produced at lower temperatures. The negative charges present in the biochar was mainly due to these two functional groups.

The surface morphology of the biochar was studied by Yadav *et al.* (2016) by adopting the SEM and XRD techniques. While the SEM images revealed its porous surface, the XRD spectrum indicated its amorphous nature, characterised by the absence of crystalline C peaks. The carboxyl, lactones and phenol groups observed from the 3412 and 1616 cm^{-1} peaks were responsible for the surface acidity, whereas the presence of carbonates might have contributed to the surface alkalinity (875 and 803 cm^{-1}). Another inference was that the alkaline functionalities of biochars were higher than their acidic functionalities, which indicated the effect of pyrolysis and nature of feedstock on the surface functionality of biochar.

In general, biochar contains very less nutrients in the order of K>N>P. The variation in the chemical make-up can be ascribed to the differences in feedstocks and pyrolysis conditions. Nitrogen content of biochar produced from poultry litter by Chan *et al.* (2007) was 20 g kg^{-1} compared to only 7.5 g kg^{-1} in biochar made from dissimilar poultry litter by Lima and Marshall (2005). The concentration of N in the feedstock and pyrolysis temperature are the reason behind such large difference noticed. Relatively much high temperature of 700°C used by Lima and Marshall (2005) for biochar production was suggestive of greater N loss.

Chan and Xu (2009) summarized the pH and nutrient profile of biochar derived from different biomass. The C content of biochar ranged from 172 - 905 g kg^{-1}. With respect to the total NPK content, the range were even wider (N: 1.8 - 56.4 g kg^{-1}, P: 2.7 - 480 g kg^{-1} and K: 1.0 - 58 g kg^{-1}).

In general, wide variation was noticed in pH of biochar. It may be as low as 4 to as high as 12, depending on the raw material, pyrolysis temperature and extent of oxidation (Cheng *et al.*, 2006; Lehmann, 2007; Chan and Xu, 2009). However, biochars are mostly basic in nature. With an increase in pyrolysis temperature, the EC value increases and the higher value is probably due to the salts of Na, K, Mg, Ca, and CO_3^{2-}. The pH values of poultry litter and its biochar was measured as 7.56 and 9.05, respectively by Sikder and Joardar (2018), which showed 19.71 per cent increase of pH value in biochar when poultry litter was pyrolyzed at 300°C.

Biochar yield from rice straw was 29.7 per cent on an average with an ash content of 34.2 per cent, bulk density of 0.75 Mg m^{-3}, pH (9.3) and high P (738 mg kg^{-1}). The CEC was high (44.2 cmol (+) kg^{-1}) and was also rich in exchangeable based mainly K as compared to Ca and Mg (Kamara *et al.*, 2015).

Shenbagavalli and Mahimairaja (2012) evaluated the prosopis biochar and reported that it had a bulk density of 0.45 Mg m^{-3}, high WHC (131 %) and a pore space of 48 per cent. The pH and EC were 7.57 and 1.3 dS m^{-1}, respectively with CEC of 16 cmol (+) kg^{-1}. Content of C was very high (940 g kg^{-1}) and N was very low (1.12 g kg^{-1}). It also contained low amounts of P (1.06 g kg^{-1}), relatively higher amounts of K (29 g kg^{-1}) and Na (38 g kg^{-1}) than Ca (11 g kg^{-1}) and Mg (0.36 g kg^{-1}).

Prakongkep *et al.* (2013) reported that RHB was highly alkaline (pH 9.7) with a high ash content (44 %) and also a high content of Si, Na, K, Ca and Mg.

Comparison between a wood and non-wood derived biochar was performed by Mukome *et al.* (2013). They detailed that wood derived biochars had lower ash content. The surface of the walnut shell biochar, which had the highest ash content consisted mostly of plate-like structures that contributed to its high surface area. In case of biochar derived from wood, the surface area correlated well with pyrolysis temperature. Irrespective of the raw material, all biochar possessed similar characteristics of high pH and high C: N ratio. Significant differences in the elemental concentration of C, N, O and H were also observed, clearly separating the biochars into wood and non-wood derived. Further they concluded that, temperature was the best predictor for surface area, when a single feedstock was considered.

Elangovan (2014) produced and characterized biochar from different feedstock and reported that biochar recovery ranged between 15.5 and 40.6 per cent. The wood and stalk biochars registered higher physical properties, alkaline in reaction, moderately saline with higher CEC, TOC, C: N ratio and nutrients than the biochar derived from dry matter biomass. Prosopis wood biochar was found superior to rest of biochar prepared. Gokila and Baskar (2015) also observed superior properties for prosopis biochar. Furthermore, they reported that with an increase in pyrolysis temperature, the biochar yield decreased and C content increased.

Biochar from three materials were compared for its properties by Akshatha (2015). Bulk density of 0.31, 0.61 and 0.53 Mg m^{-3} was recorded in wood (WB), bamboo (BB) and rice husk biochar (RHB), respectively. Maximum WHC was higher (213.31 %) in WB followed by RHB (131.41 %) and BB (93.71 %). While the biochar produced from wood and bamboo recorded higher pH, biochar from rice husk recorded lower pH. Higher EC value of 4.99 dS m^{-1} was observed in WB and lower EC values of 1.98 and 1.62 dS m^{-1} were recorded in BB and RHB respectively. Biochar produced from wood, bamboo and rice husk registered a CEC of 26.25, 23.43 and 38.63 cmol (+) kg^{-1} each, $CaCO_3$ equivalent of 31.00, 27.50 and 30.5 per cent each and C content of 72.50, 75.50 and 39.33 per cent, respectively. Higher exchangeable bases, Mn and Cu were recorded in WB while higher P, Si, Zn and Fe were recorded in RHB.

Biochar produced from tender coconut husk by Dainy (2015) had an alkaline pH (9.13), high surface area (157.93 m^2 g^{-1}) and CEC (15.26 cmol kg^{-1}). Content of C, N, P, K, Ca, Mg and S of the biochar were 72.3, 1.05, 0.38, 2.27, 0.40, 0.24 and 0.20 per cent, respectively. Very high WHC (226 per cent) and low bulk density (0.14 Mg m^{-3}) were the notable physical properties.

Investigation carried out by Usman *et al.* (2015) to assess the influence of pyrolysis temperature (300-800°C) on chemical make-up and surface chemistry of biochar showed that, fixed C, ash and basic cations of biochar increased while elements such as O, H, N and S decreased with increasing pyrolysis temperature. Together with the surface basicity, pH and pHzpc of biochar also increased with the increase in pyrolysis temperature. The biochars produced at low pyrolysis temperature do possess some functional groups, whereas the aromatic functional groups in biochars were condensed with increasing pyrolysis temperature. Mary *et al.* (2016) reported that pea pod biochar contained high TOC (11.61 %), total negative surface ions and high WHC (200 %).

Angalaeeswari and Kamaludeen (2017) compared the properties of coconut shell biochar (CSB) and mesquite wood biochar (MWB), of which the CSB had higher CEC of 11.93 cmol (+) kg^{-1}, zeta potential of -42.2mV compared to MWB. The CSB was more negatively charged than MWB, attributable to the presence of higher amount of functional groups. The pH of the CSB and MWB was alkaline (8.6 and 8.7) with an EC of 0.98 and 2.2 dS m^{-1}, respectively. The physical properties like

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bulk density, particle density, moisture and ash content of CSB (0.54, 0.25, 0.43 and 1.46 %) were higher compared to MWB (0.34, 0.23, 0.35 1.29 %) but pore space was lower (31.01 %) in comparison with the CSB (37.3 %). On the other hand, total organic C content (9.52 %) was more in CSB compared to MWB (8.90 %).

Biochar as carbon sequestrant

One of the most attractive quality of the biochar is its potential to sequester atmospheric C for centuries. Any material to serve as a C sequestrant it should possess long MRT and high resistance to oxidation and reduction processes. Several researchers are of suggestive that biochar meets the above requisite as it is protected from further oxidation. Such partially burnt products, more often called black C, may act as an important long term C sink because of its slow transformation and decomposition. In addition, it has been observed to inhibit the release of GHGs from soil, thereby reducing net emissions of GHGs as a side effect of C sequestration. Mukherjee *et al.* (2014) found that addition of biochar even produced a net negative GWP effect. Sequestration of C using biochar employs, photosynthesis to pull C from the atmosphere, and pyrolysis to convert the photosynthetically sequestered C into forms that are mostly non-degradable.

Lehmann *et al.* (2006) reported that conversion of biomass C leads to sequestration of 50 per cent of the initial C compared to the low amounts retained after burning (3 %) and biological decomposition (10-20 % in 5-10 years), therefore yielding more stable SOC than burning or direct application of biomass. The study also disclosed that around 12 per cent of the total anthropogenic C emissions by land use change could be nullified annually in the soil through biochar addition.

Decreased GHG emissions from soils have been observed following biochar application, although increased N_2O emissions have been observed in few studies (Clough *et al.*, 2010). N_2O emissions have been shown to be reduced by a variety of biochars, yet the mechanisms vary depending on soil moisture (Saarnio *et al.*, 2013) and N content and forms (vanZwieten *et al.*, 2010; Kammann *et al.*, 2012)

Knoblauch *et al.* (2011) observed that, after an incubation period of three years, only 8.5 and 4.4 per cent of the added biochar C was mineralized to CO_2 under anaerobic

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and aerobic conditions, respectively. Further they have reported that for the very same amount of C added through untreated rice husk, CO_2 released was around 34 per cent, which showed the importance of pyrolysis process.

In an incubation study conducted to examine the pattern of CO_2 emission by the application of biochar into soil, Dainy (2015) observed that 91.40 per cent reduction in CO_2 emission occurred when soil was incubated with biochar at 2 per cent (87.17 mg CO_2 100 g^{-1}) as against 2 per cent FYM (1014.05 mg CO_2 100 g^{-1}).

Carbon mineralization of different manures including biochar was studied by Benbi and Yadav (2015) and reported that mineralization was greater for rice straw and rice husk compared to rice straw compost, FYM and biochar. The proportion of predecessor C mineralized from different sources followed the order rice straw > rice husk > FYM > rice straw compost = biochar. Increasing the rate of C application (15 g C kg^{-1}) markedly increased the residence time (in days) for all the sources, except FYM, and was in the order of rice straw compost (2000) > biochar (1961) > rice husk (529) > rice straw (400). Further they concluded that rice straw and rice husk could result in short-term C increase in soil, whereas rice straw compost, biochar, and FYM may lead to long-term sequestration of C.

Results of a study conducted by Glaser *et al.* (2002) indicated that, compared to slash and burn techniques, "slash and char" significantly increased the C sequestration in soil. In a comparison study, Huang *et al.* (2018) noticed an increased C sequestration as a result of reduced CO_2 efflux in a soil applied with biochar alone, without decreasing the crop yield and net primary productivity. But Jien *et al.* (2018) disclosed that, co-application of compost with RHB significantly decreased the CO_2 emission by 13-20 per cent compared to the soil added with only compost.

Consequence of biochar application on physical properties of soil

Bulk density

In comparison with mineral soil, biochar possess very low bulk density and hence its application to soil can reduce the overall bulk density (Gundale and DeLuca, 2006; Jien and Wang, 2013; Kannan *et al.*, 2014). Mukherjee *et al.* (2014) reported that soil bulk density got reduced by 13 per cent compared to control.

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However, reduction in bulk density observed by Elangovan (2014) and Chaves *et al.* (2018) was only 5.04 and 2.32 per cent, respectively.

Results of a study conducted by Glab *et al.* (2016) indicated that biochar application significantly improved the bulk density and total porosity of sandy soil, which not only dependant on the rate but also on the size of the biochar.

Persaud *et al.* (2018) noticed a reduction of bulk density from 1.35 Mg m^{-3} in the control to 1.01 and 1.00 Mg m^{-3} for 25 and 50 t ha^{-1} of biochar, respectively. They also reported that the decrease in bulk density with the biochar application could be explained as the result of incorporation of lower density biochar (0.3 Mg m^{-3}) with a soil which had a comparatively high bulk density (1.35 Mg m^{-3}).

Porosity

The particles of biochar with a porosity of 70 to 90 per cent, when added to the soil increases the soil porosity concomitantly. This improvement may partly be attributable to increase in macro porosity resulting in higher air filled porosity and also to enhanced supply of O_2 to soil. Anyhow the extent of changes is decided ultimately by the porosity of biochar and its application rate.

Chaves *et al.* (2018) reported that the poultry litter biochar led to a decrease in bulk density, an increase in total porosity and also an increase in water content. Additionally, the biochar dose of 30 t ha^{-1} was superlative with respect to soil density and porosity. The higher quantity biochar amended soil exhibited higher porosity (52.45 %) than the unamended control (51.32 %), however this increase corresponded only to 2.2 per cent. Iddrisu *et al.* (2018) recorded the highest increase in air porosity of 10.6 per cent, as against control.

Surface area

As regards the surface area, biochar generally holds higher specific surface area than sand and comparable to or higher than clay. Hence, its application as amendment to soil will cause a net increase in total surface area (Downie *et al.*, 2009). The inner surface area of biochar produced under 400-1000°C was determined by Kishimoto (1985) and it ranged from 200 - 400 m^2 g^{-1}. Several researchers are of suggestion that biochar application into soil may increase the overall net soil surface area (Chan *et al.*, 2007) and consequently may improve soil water retention (Downie *et al.*, 2009) and aeration. Increase in sub-nanopore surface area by 15 per cent was also reported by Mukherjee *et al.* (2014).

Soil aggregation

In a study conducted to examine the effect of biochar application on soil aggregation, aggregate stability, and hydraulic properties of two different soils (silty clay and sandy loam), Ouyang *et al.* (2013) observed that biochar addition enhanced the macro aggregate formation and increased saturated hydraulic conductivity of the soils. The study also revealed that, for both the soil aggregation and soil water retention curves, the sandy loam soil was more sensitive to the biochar application. Accordingly, study conducted by Jien and Wang (2013) showed that biochar application increased MWD of soil aggregates from 2.6 to 4.0 cm.

With respect to aggregate stability, Liu *et al.* (2014) communicated that, when biochar was applied at 40 t ha^{-1}, the water stable aggregates (>0.25 mm) in the top soil layer (0-15 cm) increased, particularly the macro aggregates (≥2 mm) and also stated that biochar incorporation into upland red soil improved soil structure. Further they reported that, biochar significantly enhanced macro aggregate proportion by 32.79 to 69.71 per cent in surface soil. Same rate of biochar application was also responsible for 28.02 per cent increase in MWD of surface soil, in the rapeseed growth season.

Consequence of combined application of compost and rice husk biochar was studied by Jien *et al.* (2018) and they could obtain 11 per cent increase in macro aggregates (≥2mm), at the end of incubation.

Soil Water

The effect of biochar addition on plant available water in brown podzolic forest soils of three different textures namely sand, loam and clay was studied by Tryon (1948). From the results it could be inferred that, biochar had positive effect in sandy soil, no effect in loamy soil and negative effect in clayey soil. The increase in plant available water noticed in sandy soils suggests biochar as a useful tool in the rejuvenation of desert lands. Similar results of increased water availability due to

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biochar addition was also disclosed by Carvalho *et al.* (2014) and Lima *et al.* (2018). Uzoma *et al.* (2011) reported that application of cow dung biochar improved the field-saturated hydraulic conductivity of the sandy soil, thereby increasing WUE.

Dugan *et al.* (2010) visualized an increase in WHC of loamy sand in Ghana applied with maize stover and saw dust biochar. Almost identical results of improved available water content, as a result of increase in water retention capacity of soil was also stated by Chan *et al.* (2007); Peake *et al.* (2014); Ulyett *et al.* (2014); Ippolito *et al.* (2016); Iddrisu *et al.* (2018) and Persaud *et al.* (2018).

Barnes *et al.* (2014) reported that, biochar application decreased saturated hydraulic conductivity (K) by 92 and 67 per cent in sandy and organic soil, respectively, but increased K by 328 per cent in clayey soil. They also suggested that, any possible improvement of water availability to plants was dependent on soil type, biochar application rate and its characteristics.

For a loamy sand soil amended with biochar at different rates, moisture release curves were determined by Gaskin *et al.* (2007). Though there was no difference at low rates of biochar, significant difference was observed at higher rate, in comparison with control. They further stated that, at highest water potential the mean volumetric water content doubled with biochar addition.

Effect of biochar on soil physicochemical properties

Soil reaction

In the background of nutrient availability, the effect of biochar on pH is very much important (Steiner *et al.*, 2007). Significant increase in pH with biochar application was observed by several researchers worked on this line. Rondon *et al.* (2007) reported that application of biochar made from eucalyptus, containing 0.3 per cent ash registered an increase in soil pH from 5.0 to 5.4, which is much less than the increase from 4.7 to 6.6 in another experiment conducted with biochar containing high ash content. In agreement with this, Arocena and Opio (2003) and Khanna *et al.* (1994) also remarked the importance of ash in neutralizing the acidic soil. Another reason for the increase in soil pH is high surface area and porous nature of biochar that increases the CEC of soil. Similar conclusions were also drawn by Yamato *et al.*

(2006); Chan *et al.* (2007); Granatstein *et al.* (2009); Rodriguez *et al.* (2009); Laird *et al.* (2010); Nigussie *et al.* (2012); Ippolito *et al.* (2016), who measured the rises in soil pH by applying biochar to soil.

Dai *et al.* (2014), through an incubation study, monitored the change in pH after biochar addition and reported that biochar addition increased soil pH by 0.5-1 units at 1 per cent application rate and by 1-2 units at 3 per cent, by 180 days of incubation. The incubation study conducted on silty clay loam soil by Shah *et al.* (2017) showed a significant increase in pH and EC with the application of biochar 20 t ha^{-1} during all the stages of incubation, which may be due to the presence of salts in biochar. Further the results suggested that application of biochar cause considerable increase in soil reaction immediately after application but the increase was not sustained at same extent during later incubation periods. However, the pH was somehow greater for the soils amended with biochar. Similar trends of results in incubation study was also reported by Elangovan (2014) and Akshatha (2015).

Glaser *et al.* (2001; 2002) stated that the biochar application can increase the pH in highly weathered tropical soil. The liming effect of biochar on acidic Ultisols had been confirmed by Yuan and Xu (2011). Further scrutiny of the study revealed that, the liming effects of the biochar on soil acidity correlated with alkalinity of biochar, with R^2 value of 0.95. This suggests biochar alkalinity as a key factor in controlling the liming effect of biochar on acidic soils. Similar observations on increase in pH of highly weathered soil owing to biochar application was also reported by Jien and Wang (2013); Chintala *et al.* (2014) and Masud *et al.* (2014).

vanZwieten *et al.* (2010a) reported an increase in soil pH from 4.2 to 5.9 in an acidic soil as a result of biochar application. Further they reported a concomitant reduction in exchangeable Al with the application of biochar at 1 per cent. Similar observation on reduction of exchangeable aluminium and increase in soil pH, owing to biochar application was also reported by (Lin *et al.*, 2018) in red soil.

The results of study conducted by Liu and Zhang (2012) eliminated the concerns regarding the alkaline biochar application increasing the pH of alkaline soils. The results revealed that the dilution of the cations present in the biochar may decrease soil pH at the initial phase when soil is mixed with biochar. However, the

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increased cation exchange capacity of soil brought about by biochar may increase buffering ability of soil during later phases. Adding to that, the decomposition and eventual oxidation of organic matter in the soils can form the acidic materials which will partially neutralize alkalinity. Similarly, Shenbagavalli and Mahimairaja (2013) also found a decrease in pH of alkaline soil due to biochar addition.

Electrical conductivity

Release of weakly bound nutrients contained in biochar into the soil solution can cause an increase in EC (Glaser *et al.*, 2002; Gundale and DeLuca, 2006; Chan *et al.*, 2008). Nigussie *et al.* (2012) observed the highest EC value in soils treated with 10 t ha^{-1} biochar and suggested that increase in soil EC was the result of alkali carbonates and alkaline earth metals, inconsistent amounts of phosphates, sesquioxides, heavy metals and silica and very small amounts of inorganic N. Similar result of increase in EC (11 %) was also reported by Clay and Malo (2012), where maize stover biochar was added at 10 per cent.

Elangovan (2014) conducted an incubation experiment and opined that addition of biochar to soil, irrespective of its rate of application (0, 1, 2, 4, 6, 8 and 10 %) and incubation period (0, 30, 60 and 90 days) had significantly increased the EC, ranging from 0.34 to 0.99 dS m^{-1}. However, in the leaching experiment conducted, the addition of biochar to soil markedly reduced the EC of leachate, which may be due to electrostatic adsorption of nutrients on biochar particles.

Cation exchange capacity

Due to greater surface area, negative surface charge and charge density, biochar has a greater ability to adsorb cations. This makes biochar more capable of retaining nutrients and providing these nutrients to plants. Tryon (1948) and Hamdani *et al.* (2017) observed an increase upto 40 per cent of the initial CEC with biochar addition. Peng *et al.* (2011) reported that biochar addition increased CEC by 17.3 per cent. A report by Tando *et al.* (2017) showed that, CEC value of 5.16 cmol (+) kg^{-1} obtained before the study was increased to 6.02 cmol (+) kg^{-1} after the study.

Lehmann (2007) stated that, the benefit of higher CEC may be obtained without the risk of contributing to seasonal fluxes of NO_2. Jien and Wang (2013)

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noted increase in CEC from 7.41 to 10.8 cmol (+) kg^{-1} and BSP from 6.40 to 26.0 per cent. In an alkaline soil, increase in CEC due to biochar addition was reported by Shenbagavalli and Mahimairaja (2013).

Results of a study conducted by Pandit *et al.* (2017) showed that average CEC after amending with 1 and 4 per cent biochar doses were 17.1 and 29.5 cmol (+) kg^{-1}, respectively, which was significantly higher than those of unfertilized (11.2) and fertilized (12.1) control soils.

Effect of biochar on soil chemical properties

Nutrient retention

Higher nutrient retention for biochar has been reported by number of researchers and high surface area, variable charge and porous nature of biochar are stated as reason for such increased retention (Glaser *et al.*, 2002; Liang *et al.*, 2006). Results of a study conducted by Laird *et al.* (2010) showed a significant decrease in the amount of N, P, Mg and Si that leached from the biochar amended soil columns.

Through a column leaching study, Yao *et al.* (2012) found that the pepper wood biochar effectively reduced the amount of NH_4, NO_3 and PO_4 in the leachates by 34.7, 34 and 20.6 per cent, as against the unamended control. The peanut hull biochar also had an effect on reducing the NO_3^- and NH_4^+ leaching by 34 and 14 per cent respectively. As against additional phosphate got released from the soil columns, which confirmed the nutrient retention in soil by biochar. Based on the results it was concluded that the biochar effect on the plant nutrients leaching in soils was not uniform and that it varied with biochar and nutrient type.

Nutrient retention capacity of prosopis wood biochar was studied by Elangovan (2014) through a leaching study and observed that, increase in the biochar application rate had markedly reduced the concentration of ions in the soil leachate. At all levels of biochar addition the residual soil had accumulated significantly higher amount of C, available NPK and the impact was found more in subsoil.

Effect of biochar amendment on inorganic N leaching in a sandy soil was studied by Sika and Hardie (2014). Although there were strong reductions in N leaching, ranging from 12-96 per cent for NH_4^+ and NO_3^-, the amount of exchangeable NH_4^+ and NO_3^- left in the biochar amended soils was smaller than in the control soil. Furthermore, Raave *et al.* (2014) found that both N and P leaching was reduced with biochar application.

The results of the sorption study conducted by Dainy (2015) showed that tender coconut husk biochar could sorb 100 per cent NH_4^+, 90.70 per cent PO_4^{2-}, 92.00 per cent K^+, 87.00 per cent Ca^{2+}, 86.15 per cent Mg^{2+} and 91.82 per cent SO_4^{2-} when it was equilibrated with 100 ppm solutions (in 24 hours). For micronutrients, when 50 ppm Fe^{2+}, Mn^{2+}, Zn^{2+} and Cu^{2+} solutions were given, biochar could sorb 99.67, 100, 99.12 and 99.12 per cent respectively. She also concluded that the tender coconut husk biochar is a good sorber and slow releaser of nutrients.

Carbon dynamics

In general, the labile carbon pool has a greater turnover rate (shorter MRT) of several weeks / months / years as against the recalcitrant pools and thus the labile pools like microbial biomass carbon (MBC), water soluble carbon (WSC), hot water soluble carbon (HWSC), light fraction carbon (LFC) and particulate organic matter (POM) has been suggested as early indicators of the effects of land use changes on SOM quality (Gregorich *et al.*, 1994; Bolinder *et al.*, 1999; Paul *et al.*, 2001; Ghani *et al.*, 2003; Banger *et al.*, 2010).

Blair *et al.* (1995), Skjemstad *et al.* (2006) and Verma *et al.* (2010, 2013) attempted to identify labile carbon pools that are more sensitive to changes in agricultural management practices and land uses. Based on the results, SOC oxidized by 333 *mM* $KMnO_4$ (POXC) has been proposed as a useful index of labile soil C and more sensitive to the changes in cultivation or management practices compared to total SOC. This fraction of C encompasses all readily oxidizable organic components including humic materials and polysaccharides, which generally accounts for 5-30 per cent of SOC (Blair *et al.*, 1995; Blair, 2000; Graham *et al.*, 2002). Lu *et al.* (2014) reported that biochar and residue amendment could enhance the readily oxidized C.

Water soluble carbon, product of SOM decomposition, is the main source of energy for soil microorganisms, a prime source of mineralizable N, P, and S, and

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also it influences the metal ion availability in soils by forming soluble complexes (Stevenson, 1994). This fraction of SOC was found to increase with application of FYM and/or fertilizers. The WSC was 85 per cent greater in the organic treatments followed by 75 per cent more in the INM practice, whereas the accumulation was only 40 per cent more in the NPK, over the control treatment. Though it comprises only a small fraction of SOC, it acts as a buffering agent in replenishment mechanisms like desorption from soil colloids, dissolution from litter, and exudation from plant roots (McGill *et al.*, 1986).

Barnes *et al.* (2014) reported that the biochar addition significantly increased the C, in all soil materials: organic-rich from 37.85 to 42.47 per cent, clay-rich from 0.90 to 8.33 per cent and sand from 0.40 to 6.98 per cent. Increase in organic C content in virtue of biochar addition has been reported by many other authors as well (Banger *et al.*, 2010; Shenbagavalli and Mahimairaja, 2013; Elangovan, 2014; Akshatha, 2015; Dainy, 2015; Zhang *et al.*, 2016; Pandit *et al.*, 2017).

In order to investigate the dynamics of C in prosopis biochar amended soil, an incubation experiment was conducted by Shenbagavalli and Mahimairaja (2013). The results showed that the SOC increased proportionately with the rate of biochar application, and also increased at 90 days of incubation. Irrespective of the treatments, SOC decreased significantly during 90 days of incubation, the highest SOC being associated with 5 per cent biochar. Effect of biochar was initially lesser on MBC content. However, there was a steady increase in MBC content especially at 30 and 60 days, which declined gradually at 90 days. Addition of different levels of biochar increased significantly the MBC, among which biochar 5 per cent recorded the highest values at 30 and 60 days of incubation. At all stages, the SMBC contents were more with the higher rates of biochar. With respect to WSC, significant increase was observed upto 60 days followed by slight decline.

Influence of biochar on C fractions in soil under a corn-soybean rotation was evaluated by Sandhu *et al.* (2017). The results showed that, the effects of biochar treatments on WSC and WSN fractions for the 0-7.5 cm depth depended on biochar and soil type. Further the results suggested that alkaline biochar applied at 10 t ha^{-1} can increase the WSC content of acidic sandy loam soil, but the 10 t ha^{-1} rate might

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be low to substantially improve the HWSC fraction of soil. Contradictory trend was noticed by Ghani *et al.* (2003) from their experiments, where the WSC decreased in all treatments as compared to the control.

Soil microbial biomass carbon was measured during a winter wheat growing season after four consecutive years of 0, 4.5 and 9.0 t biochar per ha per year application by Zhang *et al.* (2014). Results showed that biochar application significantly increased soil MBC compared to the control treatment, and that the magnitude increased with biochar application rate.

To evaluate the changes in the organic C fractions, degraded red soil was amended with different rates of oak wood and bamboo biochar, along with a control and incubated for 372 days. The highest HWSC, LFOC, POXC, MBC and enzyme activities were measured in the lowest rates (0.5 %). Positive correlation was obtained between MBC and all C fractions, indicating that microbial activities resulted in mineralization of SOM. The lability index decreased with increasing biochar rates, the highest being in 0.5 per cent, and the lowest in 2 per cent biochar. The carbon pool index and carbon management index (CMI) increased with increasing biochar rates. Minimum increase in CMI was observed in bamboo biochar at 0.5 per cent (50.34 %) and the maximum in wood biochar at 2 per cent (286.33 %) and implied sequestration of organic C in soil (Demise *et al.*, 2014).

Carbon mineralization pattern of soils amended with biochar was studied by Granatstein *et al.* (2009) and communicated that, the percentage of C mineralization decreased as the amount of biochar additions increased. Also proposed, reduction in C mineralization was attributable to the dilution of SOC with C that is biologically inert. Vasu (2015) from his study shared that, application of biochar along with FYM in black soils resulted in higher carbon mineralization (192 mg kg^{-1}) and that lowest amount of CO_2 (145 mg kg^{-1}) was released from soil with only biochar application. Similar trends were also observed in red and alluvial soils studied.

In a study conducted by Qayyum *et al.* (2014), three soils were amended with biochar and wheat straw and incubated for 365 days. Biochar and wheat straw found to increase the soil C content significantly. Among SOM density fractions, higher C contents were documented in the free fraction and intra-aggregate fraction from biochar treatments as compared to the wheat straw treatment.

Ippolito *et al.* (2016) reported that increased rate of biochar application (88 % C) raised the SOC content and remained elevated over time. CO_2 evolution was also found to be increased with increasing rate of biochar, yet the CO_2 release decreased over time. Following the six-month incubation period, SOC content for the 1, 2 and 10 per cent biochar rates were 1.4, 1.9 and 6 times higher than that of the control.

Nitrogen dynamics

A major share of soil N exists in organic form. Although the soil inorganic nitrogen constitutes only a little amount of the total N (<10 %), it is the available form for plant growth, and serves as a common source of various N losses, such as volatilization, nitrification-denitrification and leaching (Haynes, 2005). Under certain conditions, SON accounts for around 90 per cent of the total N; thus, the organic N alteration plays an important role in supplying N for crop growth and in minimizing N loss. Soil organic N comprises various N compounds ranging from high-molecular-weight polyphenol-bound N to low-molecular-weight amino acids, of which soil amino acid N accounts for a large proportion. Due to their higher turnover rate, soil amino acids are rapidly mineralized and immobilized by soil microorganisms and hence it is an important storage pool for immobilized N and a dominant transitional available N form (Lu *et al.*, 2018)

Even though NO_3^- and NH_4^+ are both nitrogenous compounds, the effectiveness of biochar on N leaching varies greatly between these two inorganic N fractions, as well as between different types of biochar, it being selective in its sorption. Another factor that influences the effect of biochar in soil is its C: N ratio. Inorganic N will be effectively converted to organic N when the biochar used has a C: N ratio of at least 32:1. At the same time, such a wide C: N ratio reduces the decomposition rate of biochar. It is because the N in biochar gets condensed into heterocyclic aromatic compounds, which is biologically unavailable.

A study conducted by Shenbagavalli and Mahimairaja (2013) revealed that, the NH_4-N increased up to 60 days of incubation followed by a decrease in the soil without any treatment. Whereas, the NH_4-N content decreased gradually throughout the incubation period in the soil applied with biochar at different levels (1-5 %). An analogous trend was noticed in NO_3-N content, irrespective of the treatment. At the end of the incubation period (90 days), NO_3-N decreased to 30 mg kg^{-1} in the soil applied with biochar at 5 per cent. They assigned the reduction to be due to the adsorption of NH_4^+ on to the biochar particles and microbial immobilization or denitrification. Similar results and conclusions were also arrived at by Vasu (2015) for NH_4-N and Granatstein *et al.* (2009), DeLuca *et al.* (2009), Kolb *et al.* (2009), Singh *et al.* (2010), Ippolito *et al.* (2016) and Jien *et al.* (2018) for NO_3-N.

Wang *et al.* (2017) reported that application of biochar appeared to influence the quantity of NH_4-N and NO_3-N in an acidic soil. The concentration of NH_4-N reached a maximum value (34.0 mg kg^{-1}) at 7th day and then decreased to a much smaller concentration (5.97 mg kg^{-1}) after 14 days. Decrease in NH_4-N content was calculated as 17-60 per cent, whereas, NO_3-N content decreased by around 41-97 per cent over the entire incubation period.

In contrast, Jha *et al.* (2016) reported that addition of leucaena biochar increased the NO_3-N concentration by threefold and fivefold with the application rate of 2 and 4 per cent, respectively. Likewise, Hu *et al.* (2014) also reported that NO_3-N in soil was continually increased during 15 months after biochar addition as a result of the 10 per cent enhanced gross nitrification rate over control.

Laboratory experiment was carried out by Widowati *et al.* (2011) to examine the release pattern of N from urea mixed with biochar. For this purpose, soil was put in a 30 cm length column and fertilized with urea (300 kg ha^{-1}), with and without biochar. The results showed that biochar application could impede the conversion of NH_4 to NO_3. After 28 days of incubation, there was around 60 (chicken manure biochar) and 52 (city compost biochar) mg kg^{-1} NH_4-N, compared to 12 mg kg^{-1} in control. Leaching of N from biochar amended soil was only 470-510 mg, whereas, that from unamend soil was 641 mg. At the initial phase of incubation, application of biochar did not influence the release pattern of N. However, after two weeks of incubation the amount of NH_4-N in organic amendment treated soil was higher than that of control.

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Leaching is the main cause of N depletion in soil. There are umpteen number of studies showing the effectiveness of biochar in inhibiting N loss from leaching (Chan *et al.*, 2007; Hyland *et al.*, 2010; Dempster *et al.*, 2012; Elangovan, 2014; Zhao *et al.*, 2014). Zhou *et al.* (2011) stated that biochar had significantly stronger protective qualities, but the use of minimal amounts (10 t ha^{-1}) actually exacerbated N losses. Biochar was found more effective in retaining organic N compounds (88 %) than in retaining inorganic NO_3 (68 %).

Effect of biochar on available nutrient status

Higher nutrient availability for plants in biochar amended soil is the direct effect of nutrient addition by biochar and also the higher nutrient retention brought about by increased adsorption sites (Lehmann *et al.*, 2002). Long-term benefits in respect of nutrient availability includes a greater stabilization of SOM, concurrent slower release of nutrients from added organic matter, and better retention of all cations because of higher CEC (Lehmann *et al.*, 2003).

Application of bark charcoal induced positive changes in chemical properties of soil *viz.* increasing the total N and available P, CEC, exchangeable bases and BSP (Yamato *et al.*, 2006). Such changes in chemical properties of soil due to biochar addition has also been reported by Yuan and Xu (2011) for exchangeable bases, effective CEC and BSP, Yooyen *et al.* (2015) for nutrient availability, Zhang *et al.* (2016) for SOM, EC, P, K, Ca and Mn and Tando *et al.* (2017) for C and NPK.

Gaskin *et al.* (2010) conducted an experiment in a soil belonging to Ultisol deficient in base cations and found that biochar addition increased the K, Ca, and Mg availability in the surface soil. Kamara *et al.* (2015) communicated that the biochar treated soil had higher plant available P, exchangeable cations and CEC than the control soil. In contrast, Ippolito *et al.* (2016) noticed an increase in plant available P, Mn and Zn with increasing biochar application rate. However, micronutrient availability decreased over time likely due to mineral species precipitation.

Saranya *et al.* (2011) investigated the effect of combined application of biofertilizer and biochar. Sole biochar application recorded organic carbon content of 1.27 per cent. When *Azospirillum* was applied along with biochar, C content reached a pinnacle of 1.31 per cent. Available NPK was maximum in soil applied with biochar alone and it was further increased with the combined application.

Edmunds (2012) opined that biochar application did not increase the available N. In addition, the biochar N did not get mineralized to either NH_4 or NO_3. The only exchangeable cation that showed a significant increase was K, which increased from 0.49 to 1.09 cmol (+) kg^{-1} in the biochar treated soils.

Nigussie *et al.* (2012) reported that application of biochar on Cr polluted and unpolluted soils significantly increased the SOC and total N content and the highest values were observed in soils amended with maize stalk biochar (10 t ha^{-1}), which could be ascribed to the high amount of C and N in the maize stalk.

Elangovan (2014) conducted a series of field experiments to evaluate the effect of biochar on soil properties and found that continuous application of biochar (10 t) + RDF + FYM increased organic C, CEC, available NPK as against its one-time application. Such increase in chemical properties of soil was also noticed by the same researcher in an incubation study.

Ch'ng *et al.* (2014) conducted an incubation experiment to investigate the effect of organic amendments including biochar on P fractions. Amending soil with sole biochar or compost or its combined application was found to increase total P, available P, inorganic P fractions (soluble inorganic P, Al bound inorganic P, Fe bound inorganic P, redundant soluble inorganic P, and Ca bound P), and organic P. The increase in P fractions were ascribed to increased soil pH and reduced exchangeable Fe and Al, following biochar application.

Akshatha (2015) evaluated the effect of different biochar in soils that acidic, alkali and neutral in reaction. Irrespective of biochar, increased application rate increased the pH, available P, exchangeable cations and available Si content. With respect to micronutrients, marked decrease in DTPA extractable Fe and Mn were observed with application of wood biochar in acidic and neutral soil while in alkaline soil it was associated with rice husk biochar application.

A field study conducted by Sukartono *et al.* (2011) to evaluate the effect of biochar on soil fertility status in the sandy soils of Indonesia disclosed the beneficial effects of biochar. Improvement in soil properties were noticed, especially SOC, CEC, available P and exchangeable cations. Besides the above changes explained, biochar was also found to increase the biological N fixation (Rondon *et al.*, 2007).

Co-application of biochar and fertilizer is likely to increase the positive effect of biochar. Gokila and Baskar (2015) researched on this aspect and noticed that biochar (5 t ha^{-1}) + RDF enhanced the C content and availability of NPK. Similar results of improvement in soil properties through biochar addition was also remarked by Sasmita *et al.* (2017), Persaud *et al.* (2018) and Sadegh-Zadeh *et al.* (2018).

Effect of biochar on soil biological properties

Soil biota is crucial to the soil functioning and dispenses multifarious essential ecosystem services. The impacts of biochar on activity of soil biota are diverse and possible mechanisms were demonstrated by many scientists *viz.* (1) the pore structure and surfaces of biochar renders shelter for soil microbes (Saito and Marumoto, 2002; Quilliam *et al.*, 2013) (2) supplies nutrients and ions adsorbed on its surface to soil microbes for their growth (Joseph *et al.*, 2013) (3) triggers potential toxicity with environmentally persistent free radicals (Fang *et al.*, 2014) (4) alters microbial habitats by improving soil properties that are crucial for microbial growth (pH, water content and aeration) (Quilliam *et al.*, 2013) (5) instigate changes in enzyme activities that affect soil elemental cycles associated with microbes (Lehmann *et al.*, 2011; Yang *et al.*, 2016) and (6) augments the sorption and degradation of soil contaminants and decreases their bioavailability and toxicity to microbes (Thies and Rillig, 2009; Stefaniuk and Oleszczuk, 2016).

Biochar induced increase in soil microbial biomass is highly beneficial for agriculture for many reasons (Thies and Rillig, 2009). Such increase in microbial biomass with reduced microbial activity was reported by (Lehmann and Rondon, 2006), whereas, Pietikainen *et al.* (2000) remarked that biochar addition stimulated higher bacterial growth rates. Likewise, Jien and Wang (2013) noticed an increase in MBC after biochar application, from 835 to 1262 mg kg^{-1}, as against the control.

Ogawa *et al.* (1983) reported that bark charcoal powder containing a small amount of chemical fertilizer was sufficient for activating arbuscular mycorrhiza

(AM) and for root nodule formation in soybean plants. Similar results of increase in the colonization rate was observed in maize after biochar application by Yamato *et al.* (2006). Nishio (1996) remarked that root infection by AM fungi increased significantly because of adding biochar to alfalfa in a volcanic ash soil. Similarly, mycorrhizal infection got increased, when biochar was added to soil (Saito and Marumoto, 2002). Saxena *et al.* (2013), in their investigation found the highest number of PSB in the rhizosphere of plants grown in biochar amended soil.

Kolb *et al.* (2009) reported that, biochar addition affected the soil microbial activity and availability of nutrients. When added to soil, biochar caused a marked increase in microbial efficiency with a remarkable increase in basal respiration (Steiner *et al.*, 2007; 2008). Increased N fixation by diazotrophs due to biochar addition was reported by Ogawa (1994) and Rondon *et al.* (2007).

Chan *et al.* (2007) in the pot culture experiment with hard-setting chromisol found a decrease in soil tensile strength due to biochar application. The tensile strength got reduced from 64.4 to 31 kPa with 50 t ha^{-1} biochar. Based on the results, they concluded that soil tensile strength reduction made root and mycorrhizal nutrient mining more effective and also made the soil physically easier for invertebrates to move through, thus altering predator/prey dynamics. Similarly, Thies and Rillig (2009) stated that biochar does not contribute directly for soil microbial population, whereas, higher porosity of biochar creates favourable environment for microbes to make habitat in soil.

Dehydrogenase, strictly an intracellular enzyme functioning within the cells, is the measure of catabolic activity of micro-organism at anaerobic condition and widely used as a comparative index for soil microbial activity. It plays an indispensable role in biological oxidation of organic compounds and reflects microbial population. Ameloot *et al.* (2013) disclosed that the type of biochar alone had a significant effect on soil enzymatic activity. Among the biochars used, poultry litter biochar produced at 400°C and applied at 20 t ha^{-1} caused a significant increase in the activity of dehydrogenase.

Significant improvement in the dehydrogenase activity due to biochar was noticed by Shenbagavalli and Mahimairaja (2013). Initially, the activity of

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dehydrogenase varied between 6.26 and 8.34 μg g^{-1} and the maximum (11.81 μg g^{-1}) was noticed in the biochar applied soil at 60 days, which subsequently decreased.

Demise *et al.* (2014) from their studies on the effect of biochar on soil enzyme activities found an increase in urease and β-glucosidase activity. Similar results of increase in urease activity, following the addition of biochar was reported by Demise and Zhang (2015) in a degraded red soil (acidic). In contrast, phosphatase activity got decreased with increasing biochar rate.

Effect of biochar on plant growth

In contrast to conventional inorganic fertilizers, biochar also holds bioavailable nutrients that helps in enhancing the plant growth. Research conducted in both temperate and tropical climates have showed biochar's ability to increase plant growth. In a work done on a Colombian Oxisol by Major *et al.* (2005), DMP increased by 189 per cent when biochar (23.2 t ha^{-1}) was applied.

Several studies have reported the added effect of biochar on plant growth. According to vanZwieten *et al.* (2010a) the plant growth and shoot biomass of alder increased significantly in biochar treatments as against the control and to soil receiving only N application. Laird *et al.* (2009) also observed an increase in plant height in both oats and soybean with biochar addition. However, the results are variable and contradictory on this line so to say. Plant growth reduction was recorded by Glaser *et al.* (2002) and Deenik (2010), following biochar application.

Saranya *et al.* (2011) remarked that the application of biochar registered 17.7-25.8 per cent increase in shoot length. Further the effect got enhanced to the level of 19.3-27.4 per cent, when *Azospirillum* was applied along with biochar. Mutezo and Sassi (2013) reported that maize crop emergence was highest when biochar was applied with 50 per cent RDF which was closely followed by biochar alone.

Carter *et al.* (2013) opined that the biochar treatments increased the plant height, number of leaves, DMP and root biomass in all the cropping cycles in comparison to control. Around 903 per cent increase in biomass due to biochar amendment was noticed in the soil without fertilization, rather than fertilized one (483 %). Over the cropping cycles, impact of biochar got reduced; only 363 per cent biomass increase was observed in the third cropping cycle. Similar observations in different cropping cycles were also recorded by Persaud *et al.* (2018)

Results obtained from the investigations of Yilangai *et al.* (2014) showed that stem growth and fruit yield was significantly very high in tomatoes grown on beds treated with biochar than traditional beds without biochar. Studies conducted by Yooyen *et al.* (2015) and Ali and Mjeed (2017) also revealed the similar effect of biochar in soybean and chrysanthemum, respectively. Improvement in rice growth parameters as a result of rice husk and rich straw biochar application was reported by Akshatha (2015) and Kamara *et al.* (2015), respectively.

Pot culture experiment carried out by Rab *et al.* (2016) to evaluate the impact of biochar on mungbean crop showed that the maximum days for flowering and maturity were associated with control and minimum was in biochar (25 t ha^{-1}) treatment. Furthermore, they concluded that decrease in biochar levels enhanced maturity while increase in biochar levels resulted in delayed maturity.

Abbas *et al.* (2017) revealed that application of urea with biochar showed more promising results than fertilizer alone. Increase in plant height was found to be 5.2, 5.7, 6.0 and 7.0 per cent higher in the treatments receiving 7, 8, 9 and 10 per cent biochar with recommended dose of urea over control, respectively.

In a field trial, *Dalbergia sissoo* biochar (0 and 1 %) was used by Hamdani *et al.* (2017) to investigate its potential for improving wheat growth and yield, at varying fertilizer rates (0, 25, 50, 75 and 100 % RDF) in a calcareous soil. At reduced fertilizer doses, biochar application improved plant growth parameters *viz.* plant height, spike length, number of tillers $hill^{-1}$ and grain yield over the respective treatments having inorganic fertilizer without biochar.

Many studies revealed the positive effect of biochar on DMP (Glaser *et al.*, 2002; Allen *et al.*, 2003; Blackwell *et al.*, 2007; Rondon *et al.*, 2007; Sinclair *et al.*, 2009; Rajkovich *et al.*, 2012; Saxena *et al.*, 2013; Ndor *et al.*, 2016). Blackwell *et al.* (2007) observed that, application of biochar at 0.5 t ha^{-1} in mungbean crop increased biomass up to 122 per cent, whereas, Sinclair *et al.* (2009) could register 63 per cent biomass increase in soybean when 5 t biochar was applied and 29 per cent in 0.5 t ha^{-1}

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application. Glaser *et al.* (2002) found 150 per cent increased biomass in cowpea with biochar applied at 67 t ha^{-1}.

Rajkovich *et al.* (2012) from their studies found out that, biochar derived from animal manure increased biomass up to 43 per cent and corn stover biochar increased up to 30 per cent, whereas, biochar obtained from food waste decreased biomass by 92 per cent, as against the control. Similar results of increase in maize biomass (32.7 %) was also reported by Wang *et al.* (2017). An investigation on effect of co-application of fertilizer and biochar carried out by Zhu *et al.* (2015) revealed that, the DMP under NPK + biochar was 3.49 and 1.62 times greater their sole application. Lehmann *et al.* (2008) reported that the DMP of maize did not increase with any of the biochar applications rates tried, during the first year of research trial.

Several research works are suggestive of the rate of biochar application on biomass production. According to Lehmann *et al.* (2003), wood biochar application at 68-135 t C ha^{-1} resulted in 43 per cent increase of cowpea biomass. Husk and Major (2010) found that crop biomass increased to the tune of 17-20 and 17-99 per cent for soybean and forage crop, with an application rate of 3.9 t ha^{-1}. Guerena *et al.* (2015) reported that, biochar addition at 15 t ha^{-1} resulted in 164, 262 and 3575 per cent increase in root, shoot and nodule biomass, respectively.

Effect of biochar on crop productivity

Most important property of biochar is its effect on crop yields. Several studies have helped to conclude the effectiveness of biochar in enhancing the nutrient status of soil which in turn improved the soil fertility and crop productivity. Mechanisms that have been put forward to describe how biochar might benefit crop production are 1) through its inherent elemental composition, modifies the soil chemistry, 2) provides chemically reactive surfaces that alter the nutrient dynamics and/or catalyze helpful soil reactions, and 3) modifies physical properties of soil in such a way that benefit root growth and thereby water and nutrient retention and acquisition.

Increased yield with biochar application has been documented in both controlled environment and in field. Number of early studies conducted during 1990's was reviewed by Glaser *et al.* (2001) and these unveiled the significant impacts of low biochar additions on various crops. At higher rates, biochar seemed to inhibit the plant growth. In the subsequent experiments, combination of higher biochar application rates along with fertilizers increased yield in tropical Amazonian soils (Steiner *et al.*, 2007) and semi-arid regions (Ogawa *et al.*, 2006).

Cereals

The effect of co-application of biochar and fertilizer on grain yield of upland rice was studied by Asai *et al.* (2009) and the results showed that biochar application increased the grain yield. Akshatha (2015) reported that application of RHB increased straw yield by 55.18, 27.64 and 28.84 per cent in alkaline, neutral and acidic soils, respectively. Corresponding increase in rice grain yield was 12.78, 28.29 and 46.47 per cent. Increase in rice grain yield as a result of co-application of rice straw biochar and compost was also remarked by Sadegh-Zadeh *et al.* (2018).

Many scientists stated the effect of biochar on growth and yield of maize and reported a positive effect of biochar. Kimetu *et al.* (2008) found the maize yield to double after repeated biochar applications (7 t ha^{-1}) for 2 years in degraded Ultisols of Kenya. Two application rates (9.8, 18.4 t ha^{-1}) of biochar was tested by Laird *et al.* (2009) in a fertile central Iowa soil, and observed a marked increase in maize population (15 %) in the first year after application, and a non-significant increase (1.5 %) in the second year. There were no differences among the two biochar application rates. Baronti *et al.* (2010) also indicated that biochar at 10 t ha^{-1} recorded greater grain production in wheat, maize and ryegrass. Peng *et al.* (2011) reported that DMP in maize increased from 64 (no NPK) to 146 per cent (with NPK), after rice straw biochar was used as an amendment in pot culture trials. Coumaravel *et al.* (2015) reported that application of biochar at 10 t ha^{-1} together with the RDF + FYM + *Azospirillum* (2 kg ha^{-1}) had recorded notable higher maize yield.

Reports of Alburquerque *et al.* (2013) showed that application of biochar to a nutrient poor, acidic soil had little effect on wheat yield in the absence of fertilizers. Although, at the high dose of fertilizers addition of biochar resulted in around 20-30 per cent yield increase compared with the use of the fertilizers alone. Similar observations of increase in wheat yield with combined application of biochar and fertilizers was also described by Abbas *et al.* (2017) and Hamdani *et al.* (2017).

Zheng *et al.* (2010) concluded that the application of biochar increased crop yields, even in the absence of N fertilizer. For example, the yield of corn got increased by 23 per cent in the biochar alone treatments, compared to control. When the biochar application integrated with fertilizers, the yield got increased by 54 per cent in the 50 per cent NPK + biochar and 72 per cent in 100 per cent NPK + biochar treatments. Similar integrated effects have also been documented by Yamato *et al.* (2006) and Chan *et al.* (2007; 2008) in field and greenhouse experiments, respectively. The results of Steiner *et al.* (2008) revealed that in sorghum crop, biochar amended with poultry manure produced the highest crop yield (12.4 t ha^{-1}).

In tropical soils, yield increases tend to be higher, as these soils are inherently poor in soil fertility. Lehmann *et al.* (2003a) reported increased crop yields with increased biochar applications (up to 140 t C ha^{-1}) in the highly weathered soils of humid tropics. Yield increases of up to 300 per cent with higher application rates have been reported by Blackwell *et al.* (2009) in poor tropical soils. Similarly, Galinato *et al.* (2011) also reported 58 per cent increase in wheat yield due to biochar application.

Pulses

Iswaran *et al.* (1980) investigated the effect of *Rhizobium* inoculated biochar on the yield of moong bean and pea and the results shown that, the grain yield increased significantly when *Rhizobium* inoculated biochar was applied. Renner (2007) opined that biochar addition at 90 g kg^{-1} increased the yield of common bean by 46 per cent and DMP by 39 per cent over the control.

Vegetables

A pot culture study was conducted by Chan *et al.* (2007) to examine the effect of biochar on radish yield and the results revealed that the sole application of biochar did not increased the yield even at higher dose (100 t ha^{-1}). However, the application of biochar with fertilizer showed significant difference in yield and in that yield increased with the increase in biochar application rate. From the results, they concluded that biochar improved the FUE. Positive effect of biochar was reported by Rondon *et al.* (2007), including increased N fixation, 30 to 40 per cent increase in yield (bean) with biochar additions upto 50 g kg^{-1}.

An investigation was done by Dainy (2015) to analyse the effect of tender coconut husk biochar on yard long bean. Yield attributes like pod length, pod girth and pods per plant, pod yield, nutrient uptake and B:C ratio were significantly superior for the treatment which received biochar (20 t ha^{-1}) + PGPR (2 %) + RDF.

Oil seeds

Kannan *et al.* (2014) opined that the application of biochar (5 t ha^{-1}) significantly increased the pod yield of groundnut. Similarly, Yooyen *et al.* (2015) remarked that biochar addition at 20 and 30 t ha^{-1} produced soybean seeds which were 28.0 and 36.8 per cent heavier, respectively in comparison with control.

Tuber crops

Liu *et al.* (2014) from their research on the effect of biochar on sweet potato yield found that, biochar application (40 t ha^{-1}) increased the yield of sweet potato by 53.77 per cent, in comparison with no biochar treatment. Comparable was the findings of Walter and Rao (2015). They communicated that the biochar application improved the growth and yield of sweet potato by about 20 per cent, while its integration with fertilizers amplified tuber yield by 100 per cent.

According to Wilujeng *et al.* (2015) the combination of D. *lablab* residues and biochar @ 2 t ha^{-1} each resulted in higher yield of sweet potato (16.53 t ha^{-1}), the increase being 347.9 per cent as against the control.

Other crops

Revell (2011) reported that sole application of biochar did not had marked impact on pepper yield in both sandy loam and silty loam soil. However, N addition along with 2.5 per cent biochar often increased yield in both soils. This trend showed the significance of adding N fertilizer with biochar, which otherwise is not N rich.

An investigation on effect of biochar on yield and quality of cotton-maize-cowpea cropping sequence was undertaken by Elangovan (2014). Application of biochar significantly increased the growth, yield attributes, stalk and seed yield of cotton. Among the treatments, biochar (10 t ha^{-1}) + RDF + FYM recorded higher seed yield (96.22 % over control) followed by biochar (10 t ha^{-1}) + 75 per cent RDF

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+ FYM treatment (91.34 % over control) and biochar (7.5 t ha^{-1}) + RDF + FYM treatment (91.16 % over control). Similar trend was registered for maize grown in both cumulative and residual conditions.

According to the reports of Abewa *et al.* (2014), application of biochar (12 t ha^{-1}), lime (2 t ha^{-1}) and biochar (8, 4 t ha^{-1}) had 85.66, 70.63, 37.79 and 19.97 per cent yield (Teff) increase over control. Biochar combined with NP fertilizers was found to increase yield significantly compared to plots that received fertilizer or lime alone; suggesting that biochar is capable of improving fertilizer use efficiency.

Li *et al.* (2016) remarked that the fresh leaf yield of spinach was increased by 63.7 and 38.0 per cent under biochar and fertilizer application respectively than control. Meanwhile, both leaf dry biomass and total plant biomass were similar in biochar and fertilizer application, but significantly higher than control.

Effect of biochar on nutrient content and uptake

The optimum productivity of a cropping system depends on adequate supply of essential nutrients for plant growth and its uptake by plants. The presence of essential plant nutrients in biochar, its porous nature, high surface area and the ability of biochar to act as a medium for microorganisms are pointed out as the principal reasons for the betterment in soil properties leading to highest nutrient content and uptake in plants grown in biochar treated soils (Nigussie *et al.,* 2012).

Lehmann *et al.* (2003) opined that high P content and uptake of P and K, recorded with biochar application in maize could be ascribed to the high concentration of P and K in the biochar and high available P in biochar amended soil. Likewise, Lehmann and Rondon (2006) disclosed that in tropical environment, high rates of biochar addition have been related with increased nutrient uptake.

Major (2009) ascribed the increase in the uptake of micronutrient to the presence of chelated micro nutrients in the applied biochar. Further, biochar had the most significant effect on the content of secondary nutrients in the flag leaves of maize.

vanZwieten *et al.* (2010a) and Uzoma *et al.* (2011) investigated the effect of biochar on uptake of N in maize and reported that application of biochar increased the N uptake significantly. In similar fashion, rate of biochar application also affected N uptake and this was in agreement with Chan *et al.* (2007), who reported that N uptake by radish grown in biochar treated soil increased with increasing biochar application rates.

Hossain *et al.* (2010) reported that biochar application significantly increased the content of N and P in tomato. Rajkovich *et al.* (2012) remarked that the N uptake by maize in biochar applied plots was 15 per cent greater than the RDF application.

Akshatha (2015) from her investigation on the effect of biochar on growth and yield of rice found out that, the N, P, Mn, Cu and Si content of rice straw and its uptake was higher with RHB and that of K, Zn and Fe with wood biochar application in an acidic soil. While the RHB application recorded higher content and uptake in neutral soil, the wood biochar application recorded higher values in alkaline soils.

Increase in nutrient content and uptake of nutrients with biochar application was also reported by Senesi *et al.* (1983), Namgay *et al.* (2010), Sukartono *et al.* (2011) and Ndor *et al.* (2016) for maize, Nigussie *et al.* (2012) for lettuce, Masud *et al.* (2014) for soybean, Walter and Rao (2015) for sweet potato, Kucukyumuk *et al.* (2017) for pepper and Sun *et al.* (2017a) for radish.

The results of a study conducted by Abbas *et al.* (2017) showed conspicuous impact of biochar on wheat grain N concentration where maximum increase in grain N concentration was observed in the treatment of urea amended with 10 per cent biochar, accounting for 25 per cent increase in N concentration over control. Similarly, there were 23 and 20 per cent increase in concentration of N in grain in the treatments urea amended with 9 and 8 per cent biochar compared to the control. Almost similar trend was noticed in the case of N content in wheat straw. Hamdani *et al.* (2017) opined that the highest NPK contents in wheat were achieved at reduced fertilizer doses along with biochar application *i.e.* N and P content in wheat straw and grain at 50 per cent RDF, straw N and P uptake at 75 per cent RDF, grain N and K uptake at 50 per cent RDF and grain P uptake at 75 per cent RDF.

In contrast, Hankins *et al.* (2017) found a reduction in uptake of macro nutrients by corn, soybean and alfalfa in both sandy loam and silty clay soils, at higher doses of biochar (90 and 180 t ha^{-1}).

Residual effect of biochar on soil and crop

On account of its resistance to decomposition, it is believed that the positive effect of biochar will last for a long time much similar to the terra preta soil. Whilst there is no evidence that the effect of man-made biochar is similar to the natural biochar in the terra preta soil, several experiments had shown that the positive effect of biochar persists even after several years of its application

While evaluating the residual effect of biochar on N recovery and retention in soil, Steiner *et al.* (2008) found out that the retention of N in soil was significantly higher in the biochar amended plots (15.6 %) in comparison to fertilizers alone plots (9.7 %) after the second harvest. The total N recovery in grain, soil and crop residues was significantly higher in biochar (18.1 %), biochar + compost (17.4 %), compost (16.5 %) in comparison with fertilizer alone plots (10.9 %).

Consequence of a single application of biochar (0, 8 and 20 t ha^{-1}) to a Colombian savanna Oxisol for 4 years, under a maize-soybean rotation was investigated by Major *et al.* (2010). There was no increase in maize grain yield during the first year. But in 2nd, 3rd and 4th year, increase in yield to the extent of 28, 30 and 140 per cent against the control was registered in plots supplemented with biochar at 20 t ha^{-1}. Availability of Ca and Mg in soil was higher with biochar, whereas plant analysis revealed that they were limiting in this system. Soil pH increased and exchangeable acidity decreased with the biochar application. Furthermore, higher crop yield and nutrient uptake was particularly ascribed to the higher availability of Ca and Mg in soil applied with biochar.

Field experiment was carried out by Islami *et al.* (2013) to examine the yield stability of cassava after three years of biochar application. Addition of both FYM and biochar were observed to improve crop yield and soil quality. The increase in cassava yields due to FYM addition occurred only for the first year, whereas that for biochar continued until the third year. The results also revealed that until the third year cassava, biochar that was applied during first year of planting continued its efficiency to increase yield. The yield of cassava during third year treated with FYM and biochar was 32.47 Mg ha^{-1}, which was significantly higher than the first year (21.44 t ha^{-1}), explaining its potential for sustaining crop production over longer

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periods. The SOM content in the biochar treatment remained high well even after the harvest of the second year crop (25.8 as against 11.2 g kg^{-1} for control), deducing the prospects of biochar for soil C sequestration brought about by its recalcitrant nature.

Elangovan (2014) reported that the residual effect of biochar on plant growth, yield attributes, DMP, grain and haulm yields of two residual studies were noticeable in the succeeding cowpea as well and the trend of results was similar to that of cotton. The impact was more in cumulative residual cowpea than second residual cowpea. The residual effect of treatment biochar (10 t) + RDF + FYM recorded an increase in cowpea grain yield of 76.62 and 71.85 per cent over control under cumulative residual and second residual studies respectively. Remarkable improvement in the soil properties under second residual study was also recorded, wherein the application of biochar (10 t ha^{-1}) had reduced the bulk density (6.25 %) and increased the porosity (8.25 %), EC (92.86 %), organic C (46.10 %), available N (5.21 %), P (8.97 %) and K (8.18 %) over control. This proved the biochar's ability to sustain the soil fertility over long periods of time.

The results of a study conducted by Widowati *et al.* (2017) showed that residual biochar alone or in combination with different levels of K increased yield of maize. Residual biochar increased availability of N, P, K, Ca and Na in the soil and supplied enough nutrients especially P and K for the second crop as well.

To assess the potentiality and residual effect of poultry litter and its biochar, *Ipomoea aquatica* was grown consecutively for two seasons (Sikder and Joardar, 2018). Notable increase in plant growth and biomass production was observed and it was higher in poultry litter biochar treated soil than that of the poultry litter treated soil for both first and second crops.

Sara *et al.* (2018) conducted a field experiment to examine the residual influence of biochar (40, 60 and 80 t ha^{-1} + RDF) that applied formerly to an established experiment. The results suggested the strong carry over effect of biochar applied earlier on the succeeding crops of maize and also on soil properties.

Materials and Methods

3. MATERIALS AND METHODS

The present investigation titled "Aggrading lateritic soils (Ultisol) using biochar" was accomplished in three steps *viz.* 1. production and characterization of biochar, 2. an incubation experiment and 3. two field experiments to study the effect of biochar with/without inorganic fertilizers and FYM on soil productivity and to examine the direct and residual effects of biochar on soil fertility, crop productivity and crop quality of Chinese potato - cowpea based cropping sequence in Velappaya soil series. The details of experiments carried out, methods of analysis of soil and plant samples and the statistical techniques followed are described in this chapter, suitably subtitled under the following headings.

1. Production and characterization of biochar
2. Effect of biochar on carbon and nitrogen dynamics
3. Effect of biochar on crops
    1. Direct effect of biochar on Chinese potato
    2. Residual effect of biochar on cowpea
4. Direct and residual effects of biochar on soil

3.1. Production and characterization of biochar

3.1.1. Production of biochar

Super heating of biomass in the total / partial absence of oxygen at a temperature of 250-700°C in specially designed furnaces yield a product called 'biochar', a carbon rich stable solid that can remain in the soil for several thousands of years.

Equipment: The production of biochar was carried out in kiln designed and fabricated exclusively for the purpose using metallic drum of 87 cm height and 57 cm diameter (Plate 1). An inlet was provided at the top to load the input and an outlet on the bottom side to collect the pyrolysed final product. Air entry into the kiln was regulated by giving ten rectangular holes at the bottom. By attaching a 5 mm wire mesh at the bottom just above the base, separation of biochar and ash was enabled. A vent of 115 cm height was attached at the top to exhaust the smoke.

Procedure: Dried coconut husk and shells were loaded through the inlet. By positioning a wooden stick in the centre of kiln, a central vent was created. This stick was removed subsequently when the drum got fully filled up. Burning of the biomass was done by smearing a little diesel on the coconut husks. Once the intensity of smoke got reduced as evidenced from its thickness, closed the inlet to slow down the entry of air and thereby reducing the chances of husk getting burnt to ash. When the flame turned blue, closed all the holes of the kiln with mud for sustaining the smoke fully inside the drum. The time taken for formation of biochar was initially standardized. After 1.5-2 hours, the kiln was left to cool and the finished product 'biochar' was collected. Pyrolysis temperature was recorded using an Infrared thermometer and it was found to vary between 350 and 400°C throughout the process.

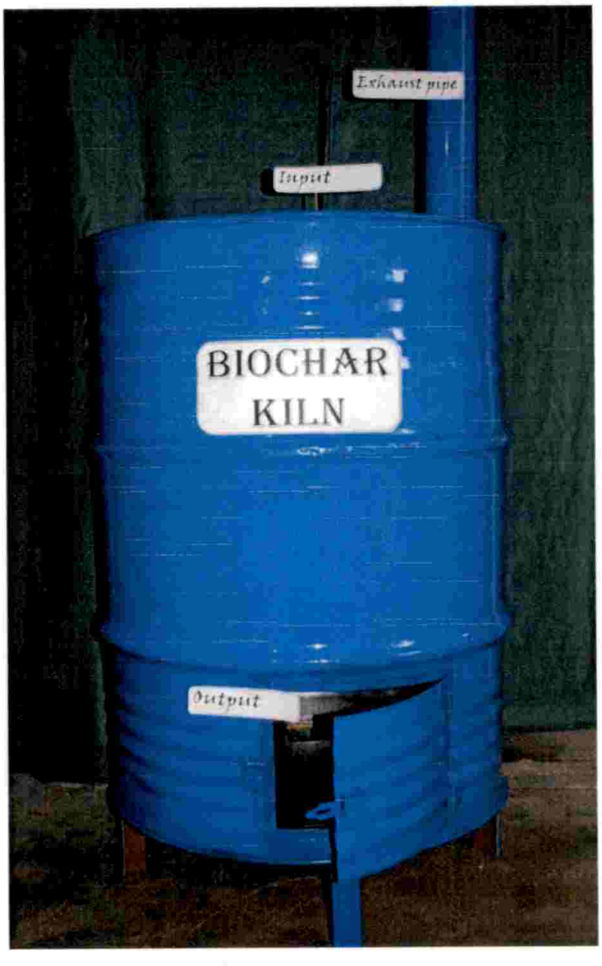

Plate 1. A view of kiln used for the production of biochar

Plate 2. Raw materials used (Coconut husk and shell)

Plate 3. Filling the drum with raw material

Plate 4. The pyrolysis process

Plate 5. Biochar inside the kiln

Plate 6. Sieving of biochar

Plate 7. Final product

Processing of biochar: The biochar was crushed using a wooden mallet and sieved through a 2 mm sieve.

The quantity of biochar that could be obtained on pyrolysis of coconut husk and shell was also recorded. A known quantity of coconut husk and shell (1:1 ratio by weight) was pyrolysed and the weight of biochar obtained was recorded. Recovery of biochar was calculated and found to be 22 per cent.

3.1.2. Characterization of biochar

pH and EC of biochar were estimated using modified dilution of 1:10 (biochar: de-ionized water) following the procedure suggested by Rajkovich *et al.* (2012). For this, biochar was shaken and equilibrated with deionized-water for an hour and the pH, EC were measured. Analysis of C, H, N, and S were carried out using CHNS analyzer (Model: Elementar Vario EL Cube). A quantity of 0.2 gram sample was weighed and digested with concentrated HNO_3 in a microwave digestion system (Model: MARSX 250/40) and made up to 100ml with double distilled water. The acid extract was fed to Inductively Coupled Plasma Optical Emission

Spectrometer (ICP-OES, Model: Optima® 8x00) for estimating nutrient content. The standard procedures adopted for analysis of biochar are given in Table 1.

Table 1. Details of analytical methods employed for biochar analysis

Characteristics	Method		Reference
	Extraction	**Estimation**	
Moisture	Gravimetric method		Jackson, 1973
Ash	Proximate analysis		Jackson, 1973
Bulk density	Cylinder method		Piper, 1966
Particle density			
Porosity			
WHC	Keen – Raczkowski Box method		Piper, 1966
pH	1: 10 ratio biochar solution	Potentiometry	Jackson, 1973 & Rajkovich *et al.*, 2012
EC		Conductometry	
CEC	Na saturation and displacement with NH_4	Flame photometry	Sumner and Miller, 1996
C	CHNS Analyzer Model: Elementar's vario EL cube		
N			
P	Microwave digestion system (HNO_3)	Colorimetry	Jackson, 1973
K		Flame photometry	Jackson, 1973
Ca		ICP-OES (Model: Optima® 8x00 series)	
Mg			
S	CHNS Analyzer Model: Elementar's vario EL cube		
Fe, Mn, Zn, Cu, B	Microwave digestion system (HNO_3)	ICP-OES (Model: Optima® 8x00 series)	

Surface acidity and basicity of biochar were estimated by following the procedure outlined by Boehm (1994). Biochar (0.3 g) was shaken with 30 ml of 0.1 *N* NaOH for 30 hours, filtered and 5 ml of the NaOH filtrate was transferred to 10 ml 0.1 *N* HCl solution that neutralized any unreacted base; the solution was back titrated with 0.1 *N* NaOH. Similarly, for surface basicity, 0.3 gram biochar was shaken with 30 ml of 0.1 *N* HCl solution for 30 hours. Further the slurry was filtered and 5 ml of HCl filtrate was transferred to 10 ml of 0.1 *N* NaOH solution, which neutralized any unreacted acid. The solution was back titrated with 0.1 *N* HCl solution. The acid or base uptake of biochar was then converted to surface basicity or acidity (mmol g^{-1}).

Cation exchange capacity of the biochar was determined using a combination of the modified ammonium acetate displacement method (Sumner and Miller, 1996) and rapid saturation diffusion method (Mulvaney *et al.*, 2004). Nearly, 0.5 gram of biochar sample was leached under vacuum with distilled water five times followed by four washes with 5 ml of 1 *M* sodium acetate (pH 8.2) and three washes with 10 ml 2-propanol. The samples were vacuum dried for 10 minutes after leaching with propanol. Four washes of 10 ml ammonium acetate were used to displace the sodium ions and the leachate was analyzed for sodium using a flame photometer. From the sodium concentration, CEC of biochar was calculated. The characteristics of biochar are given in Table 6.

The structural and surface examinations were also studied using Fourier Transform Infrared spectroscopy (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Raman spectroscopy, utilizing the facilities available at Cochin University of Science and Technology (CUSAT), Cochin and Department of Nano Science and Technology, Tamil Nadu Agricultural University (TNAU), Coimbatore.

3.2. Incubation experiment

To study the effect of biochar on soil carbon and nitrogen dynamics, an incubation experiment was carried out in the department laboratory in plastic pots of 5 kg capacity. An unfertilized surface soil was collected from F block, Agricultural Research Station, Mannuthy, where field experiment was laid out. The soil was sandy clay loam in texture, belonging to Velappaya series and Fine loamy kaolinitic, isohyperthermic, Typic plinthustults as per USDA classification. The results of initial characteristics of soil are presented in Table 7. The soil was air dried and sieved in 2 mm sieve. The treatments were imposed in the soil (1 kg) contained in 5 kg plastic pots and mixed thoroughly (Table 2). Distilled water was added to bring the gravimetric water content of the soil to field capacity. The soil samples with different treatments in triplicate were maintained separately for 15 months to simulate the duration of main and residual crop. The treatments were as follows.

T_1 : Absolute control
T_2 : FYM @ 10 t ha^{-1}
T_3 : Biochar @ 5 t ha^{-1}
T_4 : Biochar @ 7.5 t ha^{-1}
T_5 : Biochar @ 10 t ha^{-1}
T_6 : Soil test based POP + biochar 10 t ha^{-1}
T_7 : Soil test based POP

(Soil test based POP consisted of NPK and FYM 10 t ha^{-1})

Design : CRD
Treatments : 7
Replications : 3

Plate 8. Incubation experiment – an overview

The soil was incubated at field capacity for 15 months (450 days) and distilled water was added once in two days to the container to maintain a uniform moisture content throughout the incubation period. Sampling was done at fixed intervals *viz*., 0, 3, 6, 9, 12 and 15 months after incubation and analyzed for carbon and nitrogen fractions, and water holding capacity. Moisture factor was computed and applied to express the results on oven dry basis. Farm yard manure used in the study was characterized for its chemical properties by adopting the standard procedure given in Table 5 and the results are given in Table 8.

Table 2. Quantity of inorganic fertilizers, biochar and FYM applied for incubation experiment

Treatment	Treatment details
T_1	Control
T_2	FYM 4.545 g kg^{-1}
T_3	Biochar 2.273 g kg^{-1}
T_4	Biochar 3.409 g kg^{-1}
T_5	Biochar 4.545 g kg^{-1}
T_6	53.95, 50.45 and 28.02 mg kg^{-1} Urea, Rajphos and MOP + Biochar 4.545 g kg^{-1} + FYM 4.545 g kg^{-1}
T_7	53.95, 50.45 and 28.02 mg kg^{-1} Urea, Rajphos and MOP + FYM 4.545 g kg^{-1}

3.2.1. Carbon fractions

3.2.1.1. Total carbon

Total carbon content in the soil samples (passed through 0.5 mm sieve) was determined by dry combustion method, using Elemental analyser (Model: multi EA 4000).

3.2.1.2. Water soluble and Hot water soluble carbon

Water soluble carbon (WSC) and hot water soluble carbon (HWSC) were estimated as described by Ghani *et al.* (2003). Soil samples were weighed into a 100 ml polypropylene centrifuge tubes and were extracted with 30 ml of distilled water for one hour in a rotary shaker, centrifuged for 30 minutes at 10000 rpm and filtered the supernatant. From this 5 ml of supernatant was pipetted into a conical flask and treated with 5 ml of 0.07 *N* $K_2Cr_2O_7$, 10 ml of concentrated sulphuric acid and 5 ml of orthophosphoric acid. The sample was mixed carefully and digested at 150°C for 30 minutes using water bath. After 30 minutes, the contents were cooled by adding 200 ml distilled water and titrated against 0.035 *N* ferrous ammonium sulphate using diphenylamine indicator. This fraction of the SOC was classified as 'water soluble carbon' (WSC).

Further 30 ml of distilled water was added to the sediments in the same centrifuge tubes and shaken on a rotary shaker for 1 minute to suspend the soil in water. The tubes were capped and treated for 16 hours in a hot water bath at 80°C. At the end of extraction period, tubes were shaken to ensure that HWSC released from the SOM was fully suspended in the extraction medium. These tubes were centrifuged for 30 minutes, filtered and the carbon content was determined as in the case of WSC and classified as 'hot water soluble carbon' (HWSC).

3.2.1.3. Permanganate oxidizable carbon

Permanganate oxidizable carbon (POXC) was estimated as described by Blair *et al.* (1995). Finely ground air dried samples (2 g) were taken in centrifuge tube and oxidized with 25 ml of 333 *mM* potassium permanganate by shaking in mechanical shaker for 1 hour. The tubes were centrifuged for 5 minutes at 4000 rpm and 0.1 ml of supernatant solution was diluted to 25 ml with double distilled water, the concentration of $KMnO_4$ was measured at 565 nm wavelength using spectrophotometer. The change in concentration of $KMnO_4$ was used to estimate the amount of organic carbon oxidized assuming that 1.0 *mM* of MnO_4 was consumed (Mn^{7+} - Mn^{4+}) in the oxidation of 0.75 mM (9.0 mg) of carbon.

3.2.1.4. Microbial biomass carbon

Microbial biomass carbon (MBC) was measured by chloroform fumigation extraction method as suggested by Jenkinson and Powlson (1976). Briefly, three sets of 10 g soil for each sample was weighed of which one was used to determine the moisture content of the soil, another for immediate extraction with 0.5 *M* K_2SO_4 and third one for fumigation studies. A beaker containing soil sample was placed in the vacuum desiccator, the inner surface of which was lined with moist filter paper. Also placed in the desiccator was 250 ml ethanol free chloroform in a glass dish containing some glass beads. The lid joint was sealed with high density vacuum grease and run the vacuum pump till the chloroform boiled for 5 minutes. Closed the outlet and kept the desiccator in darkness overnight at 25°C. On the next day, the beaker containing chloroform and lining given with filter paper was removed after releasing the vacuum slowly. Back suction was given for five minutes to remove excess / adhered chloroform and then released the vacuum slowly. Fumigated samples were extracted with 25 ml of 0.5 *M* K_2SO_4 for 30 minutes and filtered. The supernatant collected for both fumigated and non-fumigated samples were estimated for their carbon content as given for WSC. The difference in carbon content was classified as MBC.

3.2.2. Nitrogen fractions

3.2.2.1. Total N

Of the total nitrogen in soil, 90-95 per cent is existing in organic pool and the rest in mineral form. The entire nitrogen in the sample was converted to ammonium sulphate by digestion with concentrated sulphuric-salicylic acid mixture. The digested material was treated with 40 per cent NaOH and the liberated ammonia gas was collected in boric acid containing double indicator. After complete collection of ammonia, the mixture was titrated against standard sulphuric acid and total nitrogen in the sample was determined.

3.2.2.2. Inorganic forms of nitrogen

Inorganic forms of nitrogen in the soil include exchangeable NH_4 and NO_3, which are extracted with 2 *M* KCl (Keeney and Nelson, 1982). A known quantity of extract was pipetted into distillation flask, added a pinch of freshly ignited MgO and the evolved nitrogen was collected in boric acid and titrated against standard acid. This fraction of nitrogen was classified as ammoniacal nitrogen. To the same extract in distillation tube, a pinch of devardas alloy, 10 ml of 1 per cent NaOH was added and the evolved nitrogen was trapped in boric acid and titrated against standard acid. This fraction of nitrogen was classified as nitrate nitrogen.

3.2.2.3. Organic forms of nitrogen

Preparation of hydrolysate

Preparation of hydrolysate is a prerequisite for the determination of organic forms of nitrogen in soil. The hydrolysis procedure utilized is based on the observation of Bremner (1949) that maximal release of amino acid nitrogen from surface soils and nearly maximal release of total N, was obtained by hydrolysis under reflux for about 12 hours using 3 ml of 6 *M* HCl per gram of soil. Briefly, five gram of soil sample was weighed into a 1000 ml round bottom flask, added 2 drops of octyl alcohol and 20 ml of 6 *M* HCl and boiled it gently under reflux for 12 hours using heating mantle. After completion of hydrolysis, washed the reflux condenser with distilled water, cooled and filtered the hydrolysis mixture. The mixture was neutralized to pH 6.5 using NaOH. To bring the pH to about 5 and 6.5, used 5 *M* and

0.5 *M* NaOH respectively. After neutralization, the contents were diluted to known volume with washings obtained by rinsing the electrodes and stirrer several times and then stored suitably for further analysis.

Analysis of hydrolysate

Different forms of N in the neutralized hydrolysate were converted to, and estimated as, NH_3 using steam distillation unit. Methods for determining the different forms of N are outlined hereunder (Table 3). In each method, the NH_3 liberated by steam distillation was collected in boric acid containing double indicator and determined by titration with standard H_2SO_4 (Page *et al.*, 1982).

Table 3. Steam distillation methods for determining the various forms of N in a soil hydrolysate

Forms of N	Methods
Total hydrolysable N	Steam distillation with NaOH after kjeldahl digestion with K_2SO_4-$CuSO_4$ catalyst mixture
Amino acid N	Steam distillation with phosphate – borate buffer after treatment with NaOH at 100°C and with ninhydrin (pH 2.5, 100°C) to convert α amino N to NH_4

3.2.3. Water holding capacity

A known quantity of soil was allowed to fully saturate and equilibrate with water and from water held in the soil, maximum water holding capacity was determined using Keen-Raczkowski box (Piper, 1966).

3.3. Field experiment

Two field experiments were conducted to fulfill the objectives outlined. In the first experiment, Chinese potato or coleus [*Solenostemon rotundifolius* (Poir)] was selected as test crop to study the direct effect of biochar and in second experiment cowpea was grown as test crop to study the residual effect of biochar on soil properties, yield and quality of crop.

3.3.1. Location

The field experiments were conducted at the F block, Agricultural Research Station, Mannuthy, Kerala. The farm is located in the Agro Climatic Zone (ACZ) - II

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(Midland laterites), Agro-ecological Unit (AEU) – 10 (North central laterites) of Kerala at 10° 32' North latitude and 76° 10' East longitude, at an altitude of 22.5 m above MSL.

3.3.2. Soil type

The results of initial characteristics of soil are given in Table 6. The soil of the experimental site belongs to Velappaya series, a fine loamy kaolinitic, isohyperthermic soil, taxonomically Typic plinthustults. The analysis of the initial surface soil sample collected from the experimental field revealed that the soil is sandy clay loam in texture with a bulk density of 1.23 Mg m^{-3}, strongly acidic in reaction (pH 5.24) and non - saline (EC 0.053 dS m^{-1}).

3.3.3. Direct effect of biochar on soil properties, yield and quality of Chinese potato

To study the direct effect of biochar on Chinese potato, a field experiment was carried out with seven treatments.

Treatment details:

T_1 : Absolute control
T_2 : FYM @ 10 t ha^{-1}
T_3 : Biochar @ 5 t ha^{-1}
T_4 : Biochar @ 7.5 t ha^{-1}
T_5 : Biochar @ 10 t ha^{-1}
T_6 : Soil test based POP + biochar 10 t ha^{-1}
T_7 : Soil test based POP

(Soil test based POP consisted of NPK and FYM 10 t ha^{-1})

Design	: RBD
Treatments	: 7
Replications	: 3
Variety	: Nidhi
Spacing	: 30 x 15 cm
Bed size	: 2.1 x 0.6 m (3 beds / replication)
Location	: Agricultural Research Station, Mannuthy

3.3.3.1 Soil and crop management

Preparation of field for planting

Experimental area was ploughed thoroughly using power tiller and levelled. Raised beds of 2.1 x 0.6 m size were taken manually at 45 cm apart.

Planting material and variety

Cuttings of Chinese potato, variety Nidhi were procured from Model Organic Farm (MOF), Agricultural Research Station, Mannuthy. Nidhi is a high yielding variety of coleus with 5 months' duration released from Regional Agricultural Research Station (RARS), Pattambi. Planting in the main field was done on 1st August 2017.

Application of manures and fertilizers

The Package of Practices (Crops) of Kerala Agricultural University recommends 60:60:100 kg N, P_2O_5 and K_2O + 10 t FYM per hectare for Chinese potato. In order to make fertilizer application more precise, it was done based on soil test results and the quantity was calculated based on modified RDF (54.6: 22.2: 37 kg NPK per ha). Full dose of P was applied basally, whereas N and K were applied in two splits as basal (50 %) and 45 DAS (50 %). Urea (46 % N), rock phosphate (20 % P_2O_5), and muriate of potash (60 % K_2O), were used as the fertilizer source. The fertilizers, FYM (12.5 t ha^{-1}) and biochar were applied as per treatments to the respective plots and surface mixed before sowing.

Irrigation management

First irrigation was given immediately after planting the cuttings and the subsequent irrigations were given as per soil moisture status.

Gap filling

Gap filling was done 7 days after planting to maintain optimum plant population as per the recommended crop spacing.

Weed management

Hand weeding was done as and when required to make the field totally weed free.

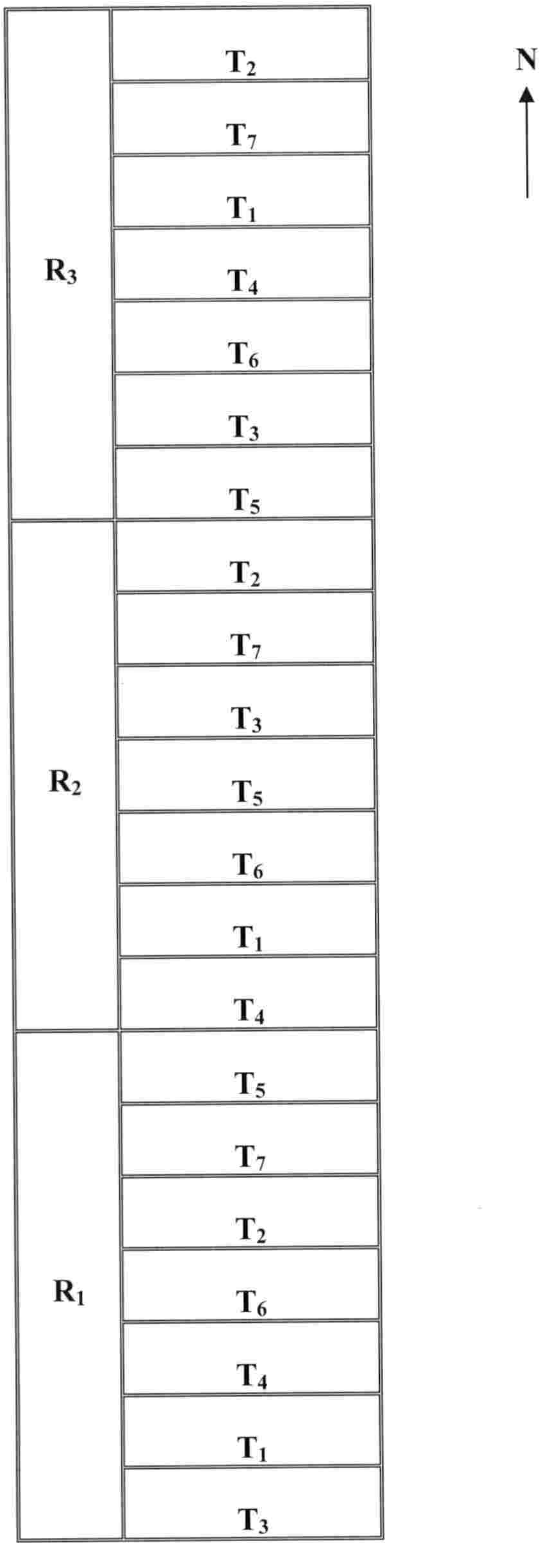

Fig. 1. Layout of the experimental field

Plate 9. Bed preparation

Plate 10. Biochar and FYM application

Plate 11. Mixing biochar and FYM with soil

Plate 12. Planting

Plate 13. Initial field view

Plate 14. Field view at flowering stage

Plate 15. Harvesting of tubers

Plate 16. Harvested tubers of Nidhi

Plant protection

Adequate plant protection measures were taken at appropriate time for the control of leaf folder and nematodes.

Harvesting

Harvesting was done five months after planting

3.3.3.2. Biometric observations

Plant height

This is the height measured from ground level to the tip of top most leaf. From each treatment height was recorded in five plants and the average value was expressed in centimeter.

Average tuber girth

The circumference of the tuber at the broadest point was measured in five medium sized tubers selected from each treatment. The mean was worked out and expressed in centimeter.

Dry matter production

Five plants were cut close to the ground level from each plot at the harvest. The samples were initially shade dried and then oven dried at 60°C till constant weight. From the dry weight of the samples collected, dry matter production (DMP) was calculated and expressed in kilograms per hectare.

3.3.3.3. Tuber yield

The plants were pulled out carefully from the plot, the tubers were separated, cleaned and the fresh weight was recorded and expressed in tons per hectare.

3.3.3.4. Assessment of tuber quality

Total carbohydrates

Total carbohydrates in the sample was found out by employing the method suggested by Sadasivam and Manickam (1992). Briefly, 0.1 g of sample was hydrolyzed with 2.5 *N* HCl for three hours and neutralized using sodium carbonate. The contents were centrifuged and the volume was made to 100 ml. From this 1 ml of aliquot was pipetted into a test tube and added 4 ml of anthrone reagent, boiled for eight minutes. This was then cooled and the green to dark green colour was read at 630 nm using a spectrophotometer. From a standard graph concentration was found and the carbohydrate content was worked out and expressed in per cent.

Protein

The protein content in the samples was found out by employing the method suggested by Sadasivam and Manickam (1992). Briefly, 0.5 g sample was weighed and ground well with a pestle and mortar in 10 ml phosphate buffer. The contents were centrifuged and from this 0.2 ml extract was pipetted into a test tube (Final volume corrected to 1 ml). To this, 5 ml of alkaline copper solution and 0.5 ml of folin-ciocalteau reagent was added and incubated in the dark at room temperature for 30 minutes. After incubation period, the intensity of blue colour developed was read at 660 nm using spectrophotometer and the protein content was calculated.

Crude fibre

Two grams of powdered dry tuber sample was treated with acid and alkali to allow oxidative hydrolytic degeneration of the native cellulose and considerable degradation of lignin, thus imitating gastric and intestinal action in the process of digestion. The residue obtained after final filtration was weighed, incinerated, cooled and weighed again. The loss in weight gave the crude fibre content (Sadasivam and Manickam, 1992).

3.3.3.5. Soil analysis

The soil sample were collected from all the treatments at the harvest stage, which also served as an initial soil sample for residual crop. The soil sample thus collected were shade dried, gently ground with wooden mallet and sieved through 2 mm sieve and stored in polythene bags and analyzed for pH, EC, organic carbon, exchangeable acidity and available nutrients *viz*., N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu and B. For the analysis of microbial biomass carbon and dehydrogenase activity, fresh soil samples were used. The analytical methods followed for the above parameters are given in Table 4.

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3.3.3.6. Plant analysis

A representative plant and tuber sample from each plot was taken for analyzing nutrient content. The samples thus collected initially air dried and then dried in hot air oven at 60°C for constant weight. The powdered samples were analyzed for total N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu and B content. The analytical methods followed are given in Table 5.

3.3.3.7. Nutrient uptake

From the nutrient content of haulm and tuber, the nutrient uptake by haulm and tuber was worked out using the given formula.

$$\text{Nutrient uptake} = \frac{\text{Nutrient content (\%) x dry matter}}{100}$$

3.3.4. Residual effect of biochar on soil properties, yield and quality of crop

To study the residual effect of biochar on growth, yield and quality of crop and on soil properties, a succeeding crop, cowpea was sown in the same field without disturbing the beds. The experimental details are as follows.

3.3.4.1. Soil and crop management

Preparation of field for sowing

Individual beds were prepared using spade to take up sowing of residual crop (cowpea) in the same layout without making any disturbance.

Planting material and variety

Cowpea, variety Bhagyalakshmy (Bush type with duration of 65-70 days) collected from Agricultural Research Station, Mannuthy was used for the study. Sowing was done on 30th November 2017.

Application of manures and fertilizers

No additional manuring and fertilizer application was done to second crop (residual) in any of the plots.

Irrigation management

Life irrigation was given on the third day after sowing and subsequent irrigations were given as per moisture status of soil.

Gap filling

Gap filling was done on 7 DAS and thinning was carried out on 15 DAS to maintain optimum plant population as per the spacing recommended.

Plate 17. Sowing of cowpea seeds

Plate 18. Field view of experimental site – residual crop (cowpea)

Weed management

Hand weeding was done as and when required to maintain weed free plots

Plant protection

Adequate plant protection measures were taken at appropriate time for the control of leaf folder, aphids and pod borer and bug to ensure healthy crop growth.

Harvesting

Pods were harvested for vegetable purpose from 45-50 days after sowing. Harvest of green, immature pods were done from all the treatments (2 pickings) and the fresh weight was recorded.

3.3.4.2. Biometric observations

Plant height

Length of individual plant from base to tip of main stem was taken as the plant height. This was recorded after harvest and expressed in centimeter.

Dry matter production

Five plants were cut to the ground level from each plot at harvest. The samples were shade dried initially and then dried in hot air oven at 60°C till the attainment of constant weight. From the dry weight of the samples collected, dry matter production (DMP) was calculated and expressed in kilograms per hectare.

Pod length

At the time of harvest, length of randomly selected five pods from each plots were measured as the distance from pedicel attachment of the pod to the apex using a scale. The mean value was computed and expressed in centimeter.

Number of pods per plant

From the five observational plants, the total numbers of pods were counted and recorded at the time of harvest.

3.3.4.3. Fresh pod yield

The yield of pods per plot recorded at each harvest was summed up and expressed as crop yield in tons per hectare.

3.3.4.4. Assessment of pod quality

Protein

The protein content in the samples was found out by employing the method suggested by Sadasivam and Manickam (1992). Briefly, 0.5 g sample was weighed and ground well with a pestle and mortar in 10 ml phosphate buffer. The contents were centrifuged and from this 0.2 ml extract was pipetted into a test tube (Final volume corrected to 1 ml). To this, 5 ml of alkaline copper solution and 0.5 ml of folin-ciocalteau reagent was added and incubated in the dark at room temperature for 30 minutes. After incubation period, the intensity of blue colour developed was read at 660 nm using spectrophotometer and the protein content was calculated.

Crude fibre

Two grams of powdered dry pod sample was treated with acid and alkali to allow oxidative hydrolytic degeneration of the native cellulose and considerable degradation of lignin, thus imitating gastric and intestinal action in the process of digestion. The residue obtained after final filtration was weighed, incinerated, cooled and weighed again. The loss in weight gave the crude fibre content (Sadasivam and Manickam, 1992).

3.3.4.5. Soil analysis

The soil sample was collected from all the treatments at the harvest stage. The soil sample thus collected were shade dried, gently ground with wooden mallet and sieved through 2 mm sieve and stored in polythene bags and analyzed for pH, EC, organic carbon, exchangeable acidity and available nutrients *viz.*, N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu and B. For the analysis of microbial biomass carbon and dehydrogenase activity fresh soil samples were used. The analytical methods followed for the above parameters are given in Table 4.

Table 4. Details of analytical methods employed for soil analysis

Characteristics	Methodology		Reference
	Extraction	Estimation	
Moisture	Gravimetric method		Jackson, 1973
Textural analysis	International pipette method		Piper, 1966
Bulk density	Cylinder method		Piper, 1966
Particle density			
Porosity			
WHC	Keen – Raczkowski Box method		Piper, 1966
pH	1: 2.5 Soil-Water suspension	Potentiometry	Jackson, 1973
EC		Conductometry	Jackson, 1973
Organic carbon	Chromic acid wet digestion method		Walkley and Black, 1934
Available N	Alkaline permanganometry		Subbiah and Asija, 1956
Available P	Bray No. 1	Colorimetry	Bray and Kurtz, 1945
Available K	Neutral Normal Ammonium Acetate	Flame photometry	Jackson, 1973
Available Ca, Mg		ICP-OES	
Available S	0.15 per cent $CaCl_2$	Turbidimetric method	Piper, 1996
Available Fe, Mn, Zn, Cu	0.1 *M* HCl	ICP-OES	Sims and Johnson, 1991
Available boron	Hot water	ICP-OES (Model: Optima® 8x00 series)	
MBC	Chloroform fumigation extraction	Wet oxidation	Jenkinson and Powlson, 1976
Dehydrogenase activity	Tri Phenyl Tetrazolium Chloride (TTC)	Tri phenyl formazan (TPF)	Casida *et al.*, 1964
Humic acid and Fulvic acid	Sequential fractionation using 0.1 *N* NaOH	Precipitation	Schnitzer, 1982

3.3.4.6. Plant analysis

A representative plant and pod sample from each plot was taken for analyzing nutrient content. The samples thus collected were dried in hot air oven at 60°C for constant moisture. The powdered samples were analyzed for total N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu and B content and the nutrient uptake by cowpea was worked out using the formula given in 3.3.3.7. The analytical methods followed for plant analysis are given in Table 5.

Table 5. Details of analytical methods employed for plant analysis

Element	Method		Reference
	Extraction	Estimation	
N	H_2SO_4-Salicylic acid digestion	Steam distillation	Bremner, 1949
P	Microwave digestion system (HNO_3)	Colorimetry	Jackson, 1973
K		Flame photometry	Jackson, 1973
Ca		ICP-OES (Model: Optima® 8x00 series)	
Mg			
S		Turbidimetry	Jackson, 1973
Fe, Mn, Zn, Cu, B		ICP-OES (Model: Optima® 8x00 series)	

3.4. Statistical analysis

The biometric observations, the analytical data of soil and plant and the computed data on uptake, yield and yield components were subjected to statistical scrutiny following the procedure outlined by Gomez and Gomez (1976), using WASP package. Correlation and regression analysis were carried out using SPSS package to determine the strength of relationship among the different soil and plant characters and also to quantify the extent of contribution and prediction towards yield, yield attributes, quality parameters, nutrient content and nutrient uptake. Path coefficient analysis was carried out using OPSTAT package.

Results

4. RESULTS

Investigations were carried out to study the carbon and nitrogen dynamics in the lateritic soil amended with biochar and also to study the direct and residual effect of biochar on soil fertility, crop productivity and crop quality of Chinese potato and cowpea based cropping sequence. The study had three parts *viz.* 1. production and characterization of biochar, 2. an incubation experiment and 3. two field experiments, of which the first one was to evaluate the direct effect of biochar on soil and crop and the second to study the residual effect of biochar. The results obtained were statistically analysed. Statistical tools like correlation, simple regression, multiple regression and path analysis were also attempted for drawing other valid conclusions. This chapter deals with the experimental results thus arrived at.

4.1. Production and characterization of biochar

Biochar used in the present study was prepared from the pyrolysis of materials with biological origin *viz.* coconut shell and husk in 1:1 ratio. Pyrolysis process was carried out in the kiln exclusively designed for the purpose (Plate 1). Biochar thus obtained was cooled, crushed, sieved through 2 mm sieve and analysed for physical, electro-chemical and chemical properties in the laboratory. The results of biochar analysis is presented in Table 6.

On an average, 22 per cent biochar could be recovered from the bio wastes. The bulk density and particle density were 0.128 Mg m^{-3} and 0.833 Mg m^{-3} respectively. The porosity value of 84.63 per cent reflected the highly porous nature. Its maximum WHC was 307.7 per cent and the ash content 11.33 per cent.

Regarding electro-chemical properties, the pH was 10.01 revealing the alkaline nature (10.01), electrical conductivity was 3.42 dS m^{-1} and cation exchange capacity 15.78 cmol (+) kg^{-1}, with potassium and calcium as the dominant cations.

Another noticeable feature of biochar was the high content of carbon, 64.14 per cent. Hydrogen was present in the biochar upto 2.08 per cent. In respect of total macronutrients, biochar contained 0.567 per cent N, 0.982 per cent P, 4.175 per cent K, 1.190 per cent Ca, 0.456 per cent Mg and 0.244 per cent S. The material had a C: N ratio of 113:1.

It also contained significant amount of micronutrients *viz.* Fe (1535 mg kg^{-1}), Mn (83.9 mg kg^{-1}), Zn (53.9 mg kg^{-1}), Cu (35.5 mg kg^{-1}) and B (55.0 mg kg^{-1}). Basicity and acidity of biochar was 2.02 and 0.08 mmol g^{-1}, respectively.

Table 6. Physical, electro-chemical and chemical properties of biochar

S. No.	Properties		Values
A. Physical properties			
1	Recovery (%)		22.0
2	Moisture (%)		10.12
3	Ash (%)		11.33
4	Bulk density (Mg m^{-3})		0.128
5	Particle density (Mg m^{-3})		0.833
6	Pore space (%)		84.63
7	Water holding capacity (%)		307.7
B. Electro-chemical properties			
1	pH		10.01
2	Electrical conductivity (dS m^{-1})		3.42
3	CEC (cmol (+) kg^{-1})		15.78
C. Chemical properties			
1	C	%	64.14
2	H		2.088
3	C:N ratio		113 : 1
4	N	%	0.567
5	P		0.982
6	K		4.175
7	Ca		1.190
8	Mg		0.456
9	S		0.244
10	Fe	mg kg^{-1}	1535
11	Mn		83.9
12	Zn		53.9
13	Cu		35.5
14	B		55.0
15	Acidity (mmol g^{-1})		0.08
16	Basicity (mmol g^{-1})		2.02

4.1.1. Surface morphology of biochar

The external and internal morphology of biochar was studied in depth using scanning electron microscope and transmission electron microscope, respectively.

4.1.1.1. Scanning Electron Microscopy

Scanning electron microscope, uses a focused beam of high energy electrons, to generate a variety of signals like backscattered electrons, secondary electrons, absorbed electrons, characteristic and continuum x-rays, *etc.* at the surface of specimens. The signals thus collected is amplified and displayed as image, which reveals the external morphological characteristics (topography) of a specimen.

Scanning electron microscope images of produced biochar, at different spatial resolutions (1-50 µm) and magnifications (500-10000) are given as Plate 19a-19e. The image exhibited a highly disordered and complex morphology with longitudinal channels and pores under higher (50 µm) magnification. The particles appeared broken resembling plant structure, with remains of vessel structure from the plant material. The pit and fall was observed on the surface. The pores were visible in different shapes and size *viz.* ellipsoidal, hollow and remained scattered over the surface. Different surface features *viz.* irregular flakes, irregular surface with polygonal shards and layered sheets were also identified. In addition, a compartmental pattern could also be seen here and there at random.

4.1.1.2. Transmission electron microscopy

The internal feature of biochar (tomography) was studied using transmission electron microscope and the micrographs of biochar at different spatial resolution are given as Plate 20a-20f. The image showed the presence of localized crystalline graphitic- like structure in the biochar. At still higher resolution, irregular globular structure was also observable. Micrographs at resolution 200 nm showed numerous black dots, indicative of carbon, the most dominant molecule of the experimental biochar.

4.1.2. Structural chemistry of biochar

Raman spectroscopy, an in-elastic scattering phenomenon, provides molecular finger prints of a material, whereas Fourier-transform infrared spectroscopy (FT-IR) is a form of vibrational spectrum, that relies on the absorbance, transmittance and reflectance of infrared light. Both Raman spectroscopy and FT-IR spectrum gives idea on the structural chemistry of a substance.

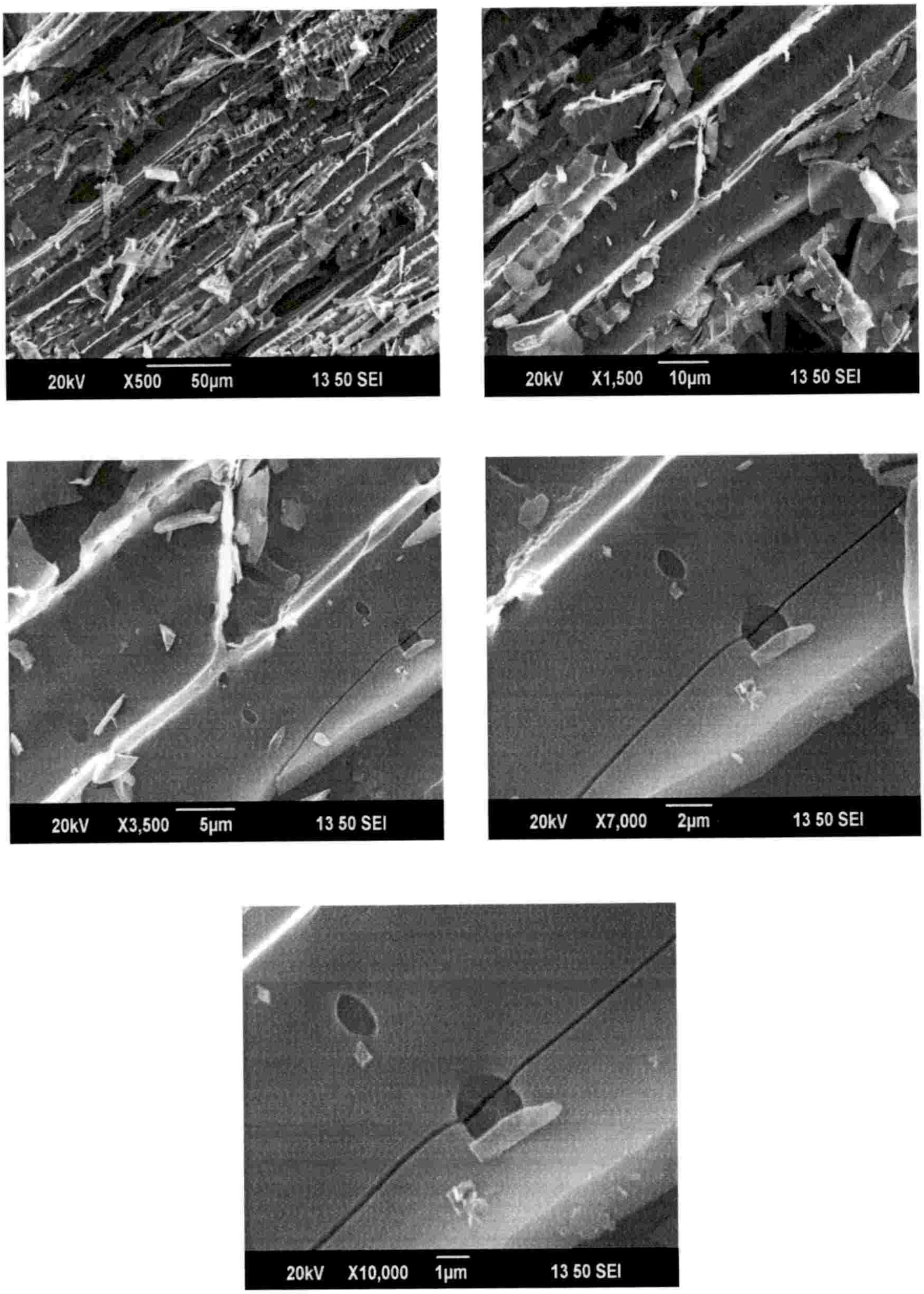

Plate 19a-19e. SEM micrographs of biochar at different spatial resolution and magnification

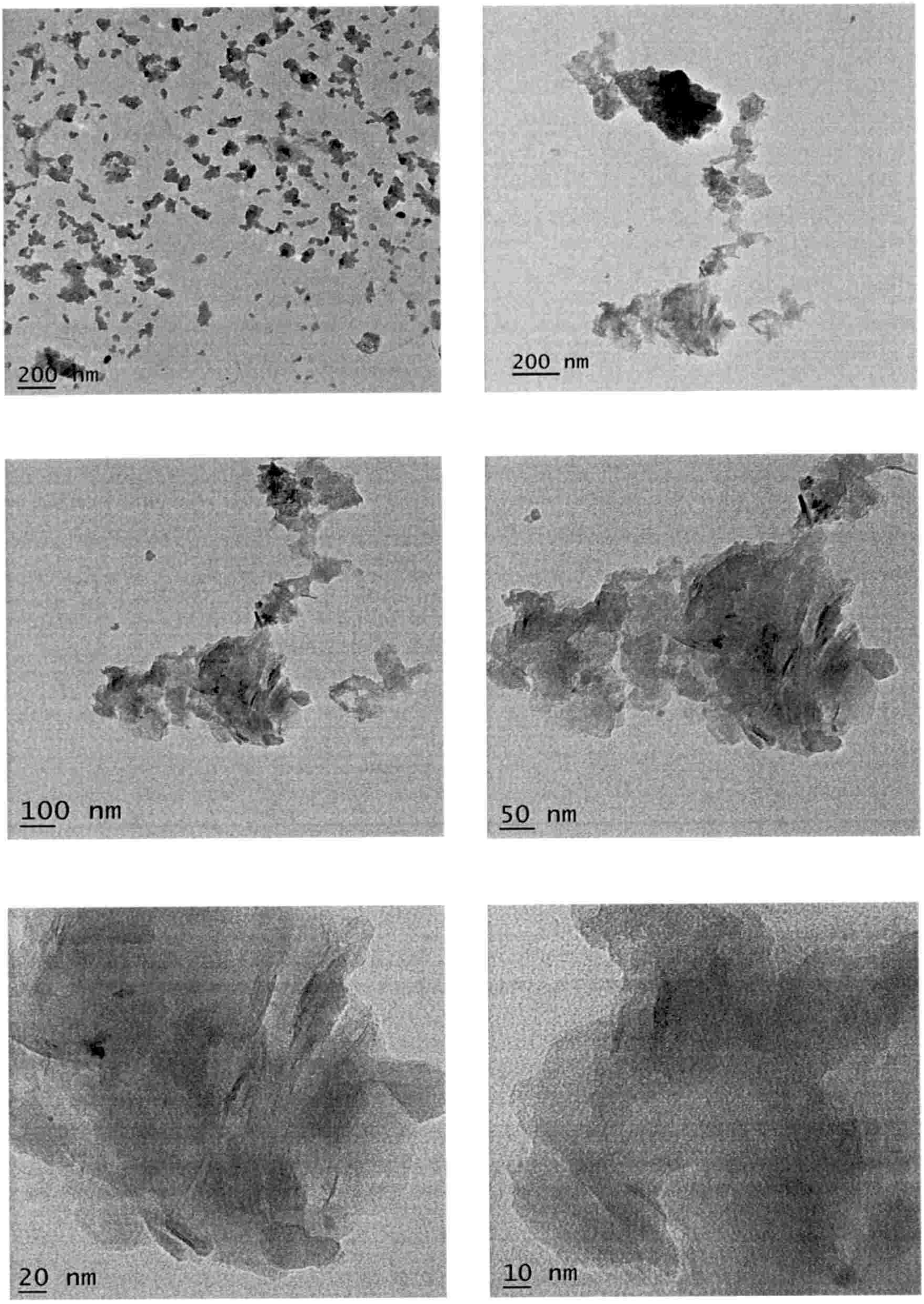

Plate 20a-20f. TEM micrographs of biochar at different spatial resolution and magnification

While the FT-IR is sensitive to hetero nuclear functional group vibration and polar bands, especially OH stretching in water, Raman spectroscopy is sensitive to homo nuclear bonds like C-C, C=C, C≡C bonds. When combined, these methods become a powerful tool to characterize any material. Hence, the structural chemistry of biochar was studied using both FT-IR and Raman spectroscopy.

4.1.2.1. Fourier-transform infrared spectroscopy

Fourier-transform infrared spectrum of biochar for functional groups is presented as Fig. 2. There were totally 13 absorption bands. The strong absorption peak at 1583.97 cm^{-1} corresponded to C=C stretching, NH_2 (amines), N=O (oxidized N functional groups), indicating that the biochar was aromatic in nature; a peak at 1394.97 and 1186.96 cm^{-1} indicated the presence of S=O (Sulfonyl chloride); a peak at 1112.23 cm^{-1} was suggestive of the presence of oxygen compounds (C-O); a peak at 3161 and 3401.13 cm^{-1} represented the presence of amines (N-H), carboxylic acids and alcoholic groups (O-H).

Additional peaks at 756.05, 810.17, 877.85 and 2919.76 cm^{-1} are attributed to alkanes (C-C, cellulose), amines (N-H) and esters of sulphur (S-OR). The peak at 618.44 cm^{-1} corresponded to C-X, where X represents halogens like Br, Cl, *etc.*, whereas the peaks at 1112.3 and 1186.96 cm^{-1} conjointly confirmed the presence of functional groups like phosphine oxide (P=O), thiocarbonyl (C=S), esters of oxygen (C-O) and alcohols (C-O).

Further the bands at 2280.2 cm^{-1} specified the presence of silicon compounds (Si-H; silane) and phosphorus compounds (P-H; phosphine).

4.1.2.2. Raman spectroscopy

The Raman spectrum of biochar is depicted as Fig. 3. Biochar reflections were produced at highly Raman shifts from 190 to 2139.5 cm^{-1}. Totally 25 Raman shifts were observed at 190, 290, 413.9, 654.5, 699.9, 797.8, 858.7, 927.1, 971.3, 1356.5, 1472, 1500, 1590, 1642, 1691, 1739, 1768, 1815, 1888.5, 1918, 1959, 1083, 2014, 2083 and 2139.5 cm^{-1}. The results of Raman spectrum were similar to that of the FT-IR spectrum, except for the peaks from 2280.2 to 3401.13 cm^{-1}, which were actually not observed in Raman spectrum.

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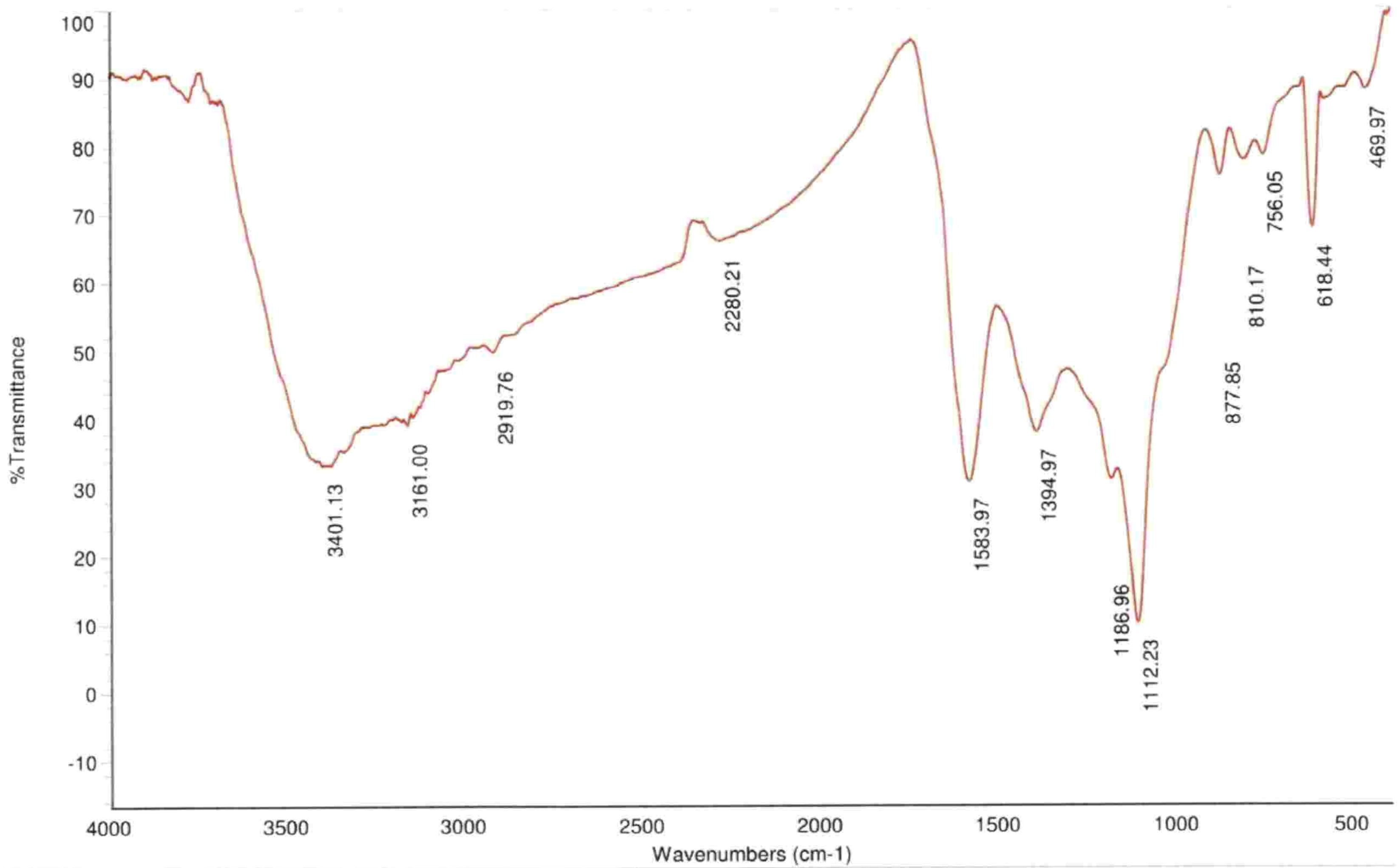

Fig. 2. Fourier-transform infrared (FT-IR) spectrum of biochar

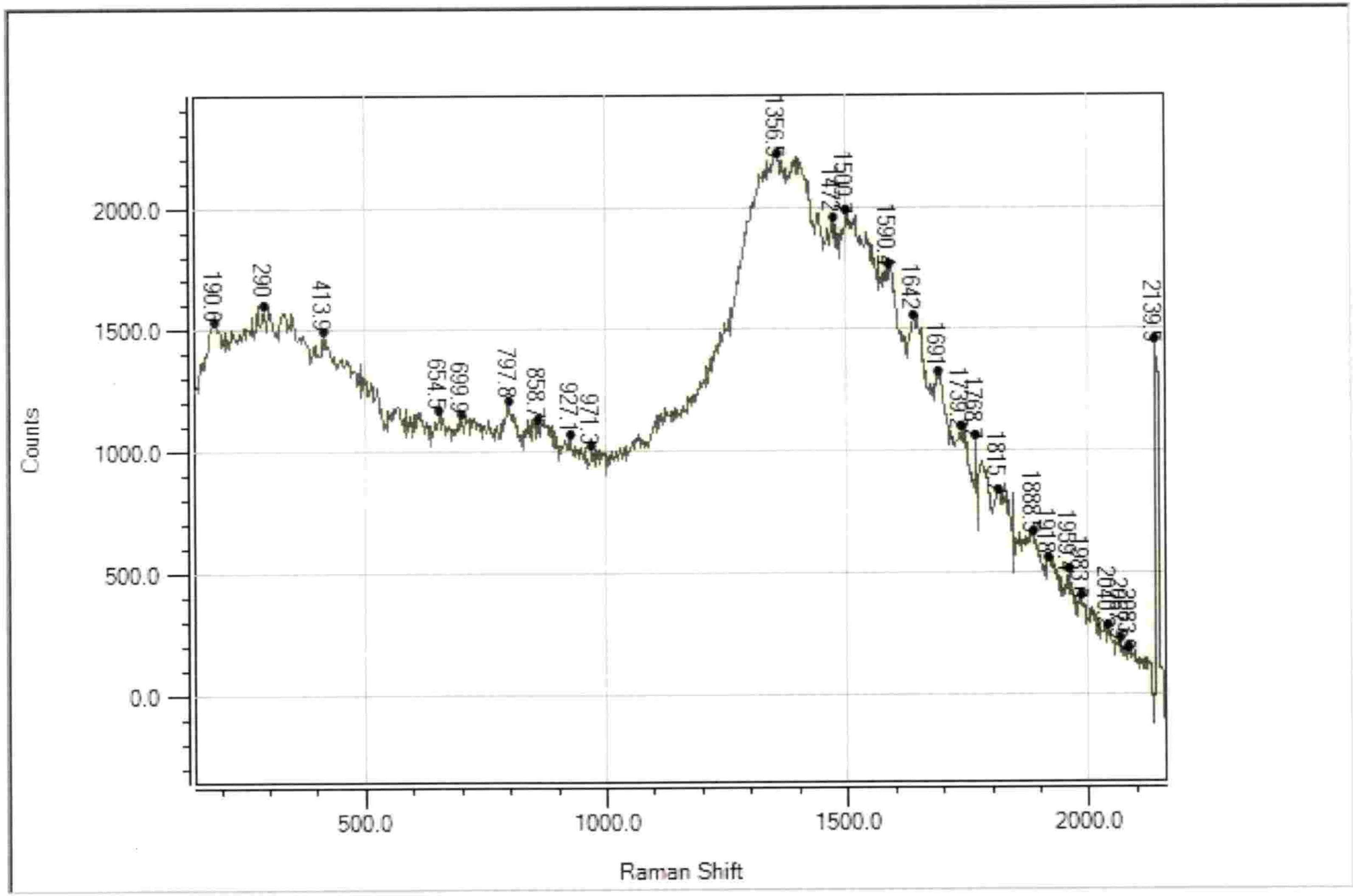

Fig. 3. Raman spectrum of biochar

The functional groups of Raman shifts are aromatic carbon C=C (1472, 1500, 1590 cm^{-1}), C=C and C=O (1642 cm^{-1}), >C=O (1691 and 1739 cm^{-1}), N=O and P-H (971.3 cm^{-1}), P-OR (927.1 cm^{-1}), aromatic ring (858.7 cm^{-1}), amines (699.9, 797.8, 858.7. 654.5 cm^{-1}), S=O (1356.5 cm^{-1}) and acyl halides (C=O, 1815 cm^{-1}).

Both the FT-IR and Raman spectrum clearly explained that the biochar was aromatic and that it contained higher amount of C, O, H and traces of N, S, P and Si on its surface.

4.2. Characterization of the experimental soil

Composite samples were collected from F block of Agricultural Research Station, Mannuthy for initial characterization and conduct of incubation experiment. The analytical results are presented in Table 7. The texture of the experimental soil was sandy clay loam with dominant proportion of sand (63.7 %) and clay (22.5 %), the silt fraction constituted to only 10 per cent. The bulk density and particle density was 1.23 and 2.27 Mg m^{-3}, respectively, which worked out to a porosity of 47.64 per cent. Maximum water holding capacity was around 30.84 per cent.

The data further showed that the soil was strongly acidic in reaction (5.24) and the electrical conductivity suggested that the soil was non-saline (0.053 dS m^{-1}). The organic carbon content was 1.55 per cent and the CEC 3.72 cmol (+) kg^{-1}.

With regard to the available nutrient status, the $KMnO_4$-N was in the low range (213.25 kg ha^{-1}), the Bray- P was medium (27.08 kg ha^{-1}) and the NH_4OAc-K was high (374.9 kg ha^{-1}). The NH_4OAc extractable calcium and magnesium were 304.4 and 59.56 mg kg^{-1} respectively and $CaCl_2$- S was 12.19 mg kg^{-1}. The soil also contained significant proportion of available micronutrients *viz.* HCl-Fe (17.59 mg kg^{-1}), HCl-Mn (46.61 mg kg^{-1}), HCl-Zn (4.67 mg kg^{-1}), HCl-Cu (2.29 mg kg^{-1}) and hot water soluble boron (0.104 mg kg^{-1}).

The dehydrogenase activity, considered as an index of general microbial activity of the soil was found to be 20.22 µg TPF g^{-1}soil 24 hr^{-1} and the microbial biomass carbon (C contained within the microbes) was 135.08 mg kg^{-1}.

Table 7. Initial characteristics of the experimental soil

S. No.	Properties		Values
A. Physical properties			
1	Mechanical composition (%)		
	Clay		22.5
	Silt		10.00
	Coarse sand		45.55
	Fine sand		18.15
2	Textural class		Sandy clay loam
3	Bulk density (Mg m^{-3})		1.23
4	Particle density (Mg m^{-3})		2.27
5	Porosity (%)		47.64
6	Water holding capacity (%)		30.84
B. Electro-chemical properties			
1	pH		5.24
2	Electrical conductivity (dS m^{-1})		0.053
3	Cation exchange capacity (cmol (+) kg^{-1})		3.72
C. Chemical properties			
1	Organic carbon (%)		1.55
2	$KMnO_4$-N	kg ha^{-1}	213.25
3	Bray-P		27.08
4	NH_4OAc-K		374.9
5	NH_4OAc-Ca	mg kg^{-1}	304.4
6	NH_4OAc-Mg		59.56
7	$CaCl_2$-S		12.19
8	HCl-Fe		17.59
9	HCl-Mn		46.61
10	HCl-Zn		4.67
11	HCl-Cu		2.29
12	Hot water soluble B		0.104
D. Biological properties			
1	Microbial biomass carbon (mg kg^{-1})		135.08
2	Dehydrogenase activity (μg TPF g^{-1}soil $24hr^{-1}$)		20.22

4.3. Chemical composition of FYM used

Farm yard manure used in the study was collected from the KVASU, Mannuthy. The dry FYM with 11.23 per cent moisture was ground to get a homogenous mass, before analysis. The composition of FYM is presented in Table 8.

Bulk density and particle density of the FYM was 0.29 and 1.05 Mg m^{-3}, respectively, which worked out to a porosity of 72 per cent. Ash content was found to be 38.13 per cent.

Table 8. Properties of Farm yard manure (FYM) used in the study

S. No.	Properties		Values
1	Moisture (%)		11.23
2	Ash (%)		38.13
3	Bulk density (Mg m^{-3})		0.29
4	Particle density (Mg m^{-3})		1.05
5	Pore space (%)		72.0
6	pH		7.70
7	Electrical conductivity (dS m^{-1})		2.023
8	Carbon (%)		30.13
9	C: N ratio		18.6 : 1
10	N	%	1.62
11	P		0.87
12	K		0.76
13	Ca		1.342
14	Mg		0.517
15	S		0.335
16	Fe	mg kg^{-1}	4738
17	Mn		669.0
18	Zn		205.0
19	Cu		25.5
20	B		9.0

It is clear from the table that the FYM was almost neutral in reaction (7.70) and non-saline (2.023 dS m^{-1}). Total carbon content was 30.13 per cent, which resulted in the C: N ratio of 18.6:1. In respect of macronutrients, FYM contained 1.62 per cent N, 0.87 per cent P, 0.76 per cent K, 1.342 per cent Ca, 0.517 per cent Mg and 0.335 per cent S. It also contained significant proportion of micronutrients *viz.* Fe (4738 mg kg^{-1}), Mn (669 mg kg^{-1}), Zn (205 mg kg^{-1}), Cu (25.5 mg kg^{-1}) and B (9.0 mg kg^{-1}).

4.4. Effect of incubation periods on carbon and nitrogen dynamics and water retention

The incubation experiment was conducted for 15 months simulating the crop duration, to study the carbon and nitrogen dynamics in soil over time and also the maximum water holding capacity. The samples were drawn at six stages *viz.* 0, 3, 6, 9, 12 and 15 months after incubation (MAI) and subjected to various analyses, the results of which are presented in the following sections.

4.4.1. Carbon fractions in soil

4.4.4.1. Total carbon

The results on statistical scrutiny of the total carbon values in the incubation experiment is presented in Table 9. As the period of incubation progressed, the total carbon content decreased initially and then increased upto 6 months of incubation, followed by a further decrease. Among the different treatments tried, soil test based POP + biochar registered the significantly higher value (2.439 %), followed by biochar at the rate of 10 t ha^{-1} (2.331 %), 7.5 t ha^{-1} (2.247 %) and 5 t ha^{-1} (2.180 %). The differences were significant. The effect of FYM and soil test based POP was comparable. Control recorded the lowest (1.983 %) value for total carbon.

The interaction of incubation period with treatments was significant. At all stages of incubation, lowest total carbon was recorded in soil alone treatment. Further, it was also observed that the effect of soil test based POP + biochar was significant during 0 and 12 months of incubation. However, there were no significant difference from other treatments, during rest of the incubation period. The effect of treatments, biochar at 10 t ha^{-1} and soil test based POP + biochar in registering higher carbon value was comparable during whole incubation period.

The simple correlation studies showed that the total carbon was positively related with C fractions *viz.* POXC (0.425**), HWSC (0.298**) and organic carbon (0.530**). Among the different nitrogen fractions NH_4-N (0.517**), THyN (0.220*), $KMnO_4$-N (0.248**) and total N (0.331**) was found to have positive relation with total carbon content (Table 10).

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Table 9. Changes in the total carbon content (%) of soil at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	2.070	1.990	2.057	1.933	1.893	1.957	**1.983**
FYM 10 t ha^{-1}	2.270	2.077	2.157	2.108	2.087	2.064	**2.127**
Biochar 5 t ha^{-1}	2.310	2.120	2.080	2.248	2.162	2.160	**2.180**
Biochar 7.5 t ha^{-1}	2.373	2.123	2.330	2.265	2.175	2.216	**2.247**
Biochar 10 t ha^{-1}	2.437	2.383	2.290	2.437	2.262	2.178	**2.331**
Soil test based POP + biochar 10 t ha^{-1}	2.727	2.340	2.280	2.538	2.437	2.313	**2.439**
Soil test based POP	2.313	2.053	2.130	2.236	2.048	1.983	**2.127**
Stage (S) mean	**2.357**	**2.155**	**2.189**	**2.252**	**2.152**	**2.124**	
	S	**T**	**T x S**				
CD (0.05)	0.045	0.049	0.119				

Table 10. Correlation between the fractions of carbon and nitrogen during incubation (n = 124)

	WSC	HWSC	POXC	MBC	OC	TC	NH_4-N	NO_3-N	THyN	AAN	$KMnO_4$-N	Total N
WSC	1.000											
HWSC	0.127^{NS}	1.000										
POXC	0.476^{**}	0.471^{**}	1.000									
MBC	0.296^{**}	-0.179^{*}	0.007^{NS}	1.000								
OC	0.419^{**}	0.340^{**}	0.720^{**}	0.252^{**}	1.000							
TC	0.097^{NS}	0.298^{**}	0.425^{**}	0.006^{NS}	0.530^{**}	1.000						
NH_4-N	0.030^{NS}	0.303^{**}	0.396^{**}	-0.328^{**}	0.317^{**}	0.517^{**}	1.000					
NO_3-N	-0.141^{NS}	-0.569^{**}	-0.246^{**}	0.423^{**}	-0.035^{NS}	-0.005^{NS}	-0.252^{**}	1.000				
THyN	0.456^{**}	-0.164^{NS}	0.417^{**}	0.412^{**}	0.540^{**}	0.220^{*}	0.323^{**}	0.262^{**}	1.000			
AAN	-0.027^{NS}	-0.519^{**}	-0.241^{**}	0.351^{**}	0.016^{NS}	0.113^{NS}	-0.042^{NS}	0.685^{**}	0.440^{**}	1.000		
$KMnO_4$-N	-0.490^{**}	-0.180^{*}	-0.198^{*}	0.239^{**}	0.016^{NS}	0.248^{**}	-0.121^{NS}	0.644^{**}	-0.018^{NS}	0.495^{**}	1.000	
Total N	0.194^{*}	0.292^{**}	0.512^{**}	0.009^{NS}	0.525^{**}	0.331^{**}	0.151^{NS}	-0.063^{NS}	0.197^{*}	-0.021^{NS}	0.138^{NS}	1.000

(WSC – Water soluble carbon, HWSC – Hot water soluble carbon, POXC – Permanganate oxidizable carbon, MBC – Microbial biomass carbon, OC – organic carbon, TC – Total carbon, THyN – Total hydrolysable N, AAN – Amino acid N)

4.4.1.2. Organic carbon

The organic carbon content of soil amended with different treatments showed significant changes not only among themselves at a particular period but also over the incubation period, with advancement (Table 11). The results showed that the organic carbon content increased during initial stages of incubation (upto 6 months) and declined subsequently. The decrease was significant during 6 to 12 months of incubation, whereas it was almost comparable at the other phases of incubation.

Irrespective of incubation period, significantly higher organic carbon content was recorded in the soil test based POP + biochar treatment (2.125 %) and the lowest was in control (1.952 %). With an increase in biochar levels, the organic carbon content increased, however, the increase was only marginal. Moreover, it was seen that the lowest organic carbon values were recorded in control during all the stages of incubation. With respect to the other treatments, there was no clear trend.

The simple correlation analysis disclosed that the organic carbon was positively correlated with all the carbon fractions *viz.* WSC (0.419^{**}), HWSC (0.340^{**}), POXC (0.720^{**}), MBC (0.252^{**}) and total carbon (0.530^{**}). Among the nitrogen fractions NH_4-N (0.317^{**}), THyN (0.540^{**}) and total N (0.525^{**}) was found to have positive relationship with organic carbon (Table 10).

The simple regression analysis to quantify the changes in organic carbon values during the period of incubation had shown that the variation in organic carbon content of different treatments could be significantly explained with number of days of incubation (Table 12). Though a decline was noticed in all the treatments, the reduction was highest in soil applied with soil test based POP (4.177 mg kg^{-1} day^{-1}). With an increase in the biochar levels, sharp reduction was noticed in the rate of decrease. When the biochar application (10 t ha^{-1}) was combined with soil test based POP, the rate of reduction got increased (2.915 mg kg^{-1} day^{-1}), in comparison with sole biochar application (2.845 mg kg^{-1} day^{-1}).

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Table 11. Changes in the organic carbon content (%) of soil at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	2.031	2.006	1.980	1.933	1.870	1.891	**1.952**
FYM 10 t ha^{-1}	2.105	2.138	2.141	2.114	2.078	1.969	**2.091**
Biochar 5 t ha^{-1}	2.021	2.114	2.121	1.993	1.951	1.914	**2.019**
Biochar 7.5 t ha^{-1}	2.079	2.119	2.138	1.953	1.957	1.980	**2.038**
Biochar 10 t ha^{-1}	2.121	2.092	2.137	2.132	1.988	2.006	**2.079**
Soil test based POP + biochar 10 t ha^{-1}	2.199	2.127	2.175	2.108	2.094	2.048	**2.125**
Soil test based POP	2.124	2.126	2.187	2.127	1.986	1.957	**2.084**
Stage (S) mean	**2.097**	**2.103**	**2.126**	**2.051**	**1.989**	**1.966**	
	S	**T**	**T x S**				
CD (0.05)	0.025	0.027	0.065				

Table 12. Simple regression analysis between organic carbon (Y) and days of incubation (X)

Treatments	R^2	a (intercept)	Rate of change (mg kg^{-1} day^{-1})
Control	0.697^{**}	20339.7	-3.657
FYM 10 t ha^{-1}	0.446^{**}	21544.9	-2.817
Biochar 5 t ha^{-1}	0.501^{**}	21011.7	-3.642
Biochar 7.5 t ha^{-1}	0.483^{**}	21207.2	-3.689
Biochar 10 t ha^{-1}	0.457^{**}	21433.9	-2.845
Soil test based POP + biochar 10 t ha^{-1}	0.552^{**}	21908.6	-2.915
Soil test based POP	0.422^{**}	21783.9	-4.177

4.4.1.3. Water soluble carbon (WSC)

The WSC content of soil as influenced by different treatments and as monitored at periodical interval is presented in Table 13. Water soluble carbon showed a trend similar to that of organic carbon. As in the case of organic carbon, the WSC increased upto 6 months of incubation and decreased thereafter. The decrease / increase during the initial phases of incubation was significant, but the decrease in last two phases of incubation was only marginal. Water soluble carbon content ranged from 92.61 to 111.5 mg kg^{-1}. Irrespective of stages, the higher WSC was recorded in FYM 10 t ha^{-1} and it was also significant. The lowest value was recorded in soil test based POP. The variation of WSC in rest of the treatments was just marginal.

From the simple correlation studies it could be concluded that, the WSC was positively related to POXC (0.476^{**}), MBC (0.296^{**}), OC (0.419^{**}), THyN (0.456^{**}) and total N (0.194^{*}), and negatively to $KMnO_4$-N (-0.490^{**}) (Table 10).

4.4.1.4. Hot water soluble carbon (HWSC)

The changes in HWSC content as influenced by treatments and days of incubation revealed that the HWSC declined over the period of incubation (Table 14). However, at the last phase of incubation (15 MAI), it showed a sharp increase, which did not exceed the initial content.

Table 13. Changes in the water soluble carbon content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	101.8	118.4	129.6	87.27	73.53	100.5	**101.8**
FYM 10 t ha^{-1}	104.0	105.6	164.3	106.2	65.06	123.7	**111.5**
Biochar 5 t ha^{-1}	100.3	82.46	131.4	99.10	55.58	87.76	**92.77**
Biochar 7.5 t ha^{-1}	97.41	113.8	155.1	126.3	72.86	54.19	**103.3**
Biochar 10 t ha^{-1}	91.89	148.0	131.6	106.9	92.38	47.24	**103.0**
Soil test based POP + biochar 10 t ha^{-1}	88.56	156.0	142.6	107.5	87.14	37.40	**103.2**
Soil test based POP	86.61	141.0	134.5	88.91	60.67	43.94	**92.61**
Stage (S) mean	**95.80**	**123.6**	**141.3**	**103.1**	**72.46**	**70.66**	
	S	**T**	**T x S**				
CD (0.05)	4.68	5.05	12.38				

Table 14. Changes in the hot water soluble carbon content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	439.6	296.5	308.2	184.1	219.9	302.3	291.8
FYM 10 t ha^{-1}	506.8	434.3	360.3	177.5	281.0	376.8	356.1
Biochar 5 t ha^{-1}	470.1	288.5	332.3	236.6	263.8	254.5	307.6
Biochar 7.5 t ha^{-1}	479.8	282.1	322.2	236.7	301.2	356.2	329.7
Biochar 10 t ha^{-1}	502.7	282.3	348.8	250.3	155.1	265.3	300.8
Soil test based POP + biochar 10 t ha^{-1}	523.6	280.5	354.9	299.4	216.3	318.2	332.2
Soil test based POP	417.9	367.1	322.2	230.1	178.5	345.6	310.2
Stage (S) mean	477.2	318.8	335.6	230.7	230.8	317.0	
	S	**T**	**T x S**				
CD (0.05)	13.2	14.3	35.0				

Irrespective of the incubation period, FYM at 10 t ha^{-1} registered the highest and significant value (356.1 mg kg^{-1}). Lowest HWSC was registered in control (291.8 mg kg^{-1}), which was on par with biochar at 10 t ha^{-1}. The treatment FYM at 10 t ha^{-1}, that registered the highest value of HWSC, also showed a significant variation among the days of incubation.

Simple correlation studies further notified the positive relationship of HWSC with POXC (0.471**), organic carbon (0.340**), total carbon (0.298**), NH_4-N (0.303**) and total N (0.292**). A negative correlation existed between MBC (-0.179*), NO_3-N (-0.569**), AAN (-0.519**) and $KMnO_4$-N (-0.180*) (Table 10).

4.4.1.5. Permanganate oxidizable carbon (POXC)

The POXC content of soil as influenced by different treatments and incubation periods is presented in Table 15. It was inferred from the results that the POXC content significantly decreased with advancement of incubation period. On an average, the POXC content at the start of experiment was 1549.8 mg kg^{-1}, which decreased to 890.2 mg kg^{-1} at the end of incubation.

Among the different treatments tried, the POXC content was comparable in soil test based POP (1360.9 mg kg^{-1}), soil test based POP + biochar (1356.6 mg kg^{-1}) and biochar at 10 t ha^{-1} (1342.0 mg kg^{-1}). The lowest was recorded in the soil alone treatment. A close scrutiny of change in POXC values in different treatments showed that the change was almost comparable in different stages of incubation.

In the case of biochar at 10 t ha^{-1}, soil test based POP + biochar and soil test based POP treatments, the decrease was significant at every stage of incubation, though the decline was only comparable between 3rd and 9th months of incubation. The interaction effect further confirmed that the POXC content was lower in the soil alone treatment, at all stages of incubation.

The simple correlation studies unveiled the positive and significant relationship of POXC with different fractions of carbon *viz.* WSC, HWSC, organic carbon, total carbon. It was further noticed that the POXC was positively related with the nitrogen fractions *viz.* NH_4-N, THyN and total N, whereas, negatively with the NO_3-N, AAN and $KMnO_4$-N (Table 10).

Table 15. Changes in the permanganate oxidizable carbon content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	1449.4	1400.5	1350.8	826.8	647.1	760.6	**1072.5**
FYM 10 t ha^{-1}	1520.1	1507.5	1421.5	1221.5	876.8	849.2	**1232.8**
Biochar 5 t ha^{-1}	1538.0	1436.8	1452.5	949.3	868.6	825.6	**1178.5**
Biochar 7.5 t ha^{-1}	1568.2	1561.1	1399.9	1103.1	1084.3	820.9	**1256.3**
Biochar 10 t ha^{-1}	1591.1	1429.8	1414.6	1442.3	1316.3	857.7	**1342.0**
Soil test based POP + biochar 10 t ha^{-1}	1626.2	1478.2	1445.2	1187.6	1315.6	1086.6	**1356.6**
Soil test based POP	1555.5	1448.5	1444.5	1387.0	1299.4	1030.8	**1360.9**
Stage (S) mean	**1549.8**	**1466.1**	**1418.4**	**1159.7**	**1058.3**	**890.2**	
	S	**T**	**T x S**				
CD (0.05)	29.6	32.0	78.4				

The rate of decrease in the POXC content was quantified by simple regression analysis, which revealed that in all the treatments, the change in POXC content could be significantly attributed to the days of incubation (Table 16). The rate of decrease was found to be maximum in the soil alone treatment (1.977 mg kg^{-1} day^{-1}) and the minimum in the soil test based POP treatment (0.993 mg kg^{-1} day^{-1}). With an increase in biochar levels, the rate of decrease got reduced. It was further noticed that when the biochar and FYM were applied along with the NPK fertilizer, there was a sharp reduction in the rate of decrease as compared to their sole application. For example, when the soil was treated with biochar alone at 10 t ha^{-1}, the rate of decrease was 1.293 mg kg^{-1} day^{-1}, which got reduced to 1.093 mg kg^{-1} day^{-1} when the biochar was applied in combination with soil test based POP.

Table 16. Simple regression analysis between POXC (Y) and days of incubation (X)

Treatments	R^2	a (intercept)	Rate of change (mg kg^{-1} day^{-1})
Control	0.822**	1517.4	-1.977
FYM 10 t ha^{-1}	0.897**	1621.8	-1.729
Biochar 5 t ha^{-1}	0.871**	1590.6	-1.832
Biochar 7.5 t ha^{-1}	0.930**	1646.5	-1.735
Biochar 10 t ha^{-1}	0.681**	1626.3	-1.263
Soil test based POP + biochar 10 t ha^{-1}	0.790**	1602.5	-1.093
Soil test based POP	0.768**	1584.4	-0.993

4.4.1.6. Microbial biomass carbon (MBC)

The MBC content of soil as influenced by treatments and days of incubation is presented in Table 17. Irrespective of stage, the MBC was found to be the highest in the soil applied with soil test based POP (136.2 mg kg^{-1}) and biochar at 10 t ha^{-1} (133.2 mg kg^{-1}), which were on par with each other. As expected, the lowest MBC was recorded in soil alone treatment (80.40 mg kg^{-1}). With an increase in the levels of biochar, the MBC content also increased.

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Table 17. Changes in the microbial biomass carbon content (mg kg^{-1}) at different stages of incubation

Treatments	**Incubation period (months)**						**Treatment (T) mean**
	0	**3**	**6**	**9**	**12**	**15**	
Control	64.82	77.21	103.77	92.95	79.61	64.02	**80.40**
FYM 10 t ha^{-1}	68.60	98.51	172.95	93.67	104.22	96.07	**105.67**
Biochar 5 t ha^{-1}	69.30	78.36	129.57	120.34	92.53	144.54	**105.77**
Biochar 7.5 t ha^{-1}	67.36	87.27	126.16	117.27	105.18	169.87	**112.19**
Biochar 10 t ha^{-1}	73.00	115.79	228.34	105.48	150.55	125.86	**133.17**
Soil test based POP + biochar 10 t ha^{-1}	78.05	113.79	187.44	100.96	115.08	113.53	**118.14**
Soil test based POP	72.68	137.13	285.46	108.53	104.20	109.35	**136.22**
Stage (S) mean	**70.54**	**101.15**	**176.24**	**105.60**	**107.34**	**117.61**	
	S	**T**	**T x S**				
CD (0.05)	6.15	6.65	16.28				

With an advancement of incubation period, the MBC content increased and reached a maximum at 6 months (176.3 mg kg^{-1}) and declined thereafter to 117.6 mg kg^{-1} at 15 months of incubation. The value was higher than the initial sampling at all stages. Though there were significant variation among treatments upto 9 months of incubation, it was not marked towards the last phases of incubation.

The interaction of incubation period with treatments was significant. At all stages of incubation, lowest MBC was recorded in control. Though there were no marked differences initially, with an advancement in incubation period significant differences were noticed among the treatments. Further it was observed that in all the treatments, except control, the lowest MBC was registered during the 0th month of incubation.

Through the simple correlation studies, the positive relationship was noticed between the MBC and WSC (0.296^{**}), organic carbon (0.252^{**}), NO_3-N (0.423^{**}), THyN (0.412^{**}), AAN (0.351^{**}) and $KMnO_4$-N (0.239^{**}). The relationship between MBC and HWSC (-0.179^{*}) and NH_4-N (-0.328^{**}) was negative (Table 10).

4.4.2. Nitrogen fractions in soil

4.4.2.1. Inorganic nitrogen fractions

4.4.2.1.1. Ammoniacal nitrogen (NH_4-N)

The NH_4-N fraction was found to be higher in the soil applied with soil test based POP + biochar (33.49 mg kg^{-1}) and soil test based POP (33.46 mg kg^{-1}), which were on par (Table 18). The effect of other treatments on NH_4-N fraction was comparable, though significantly higher than the control. The NH_4-N was lowest in the soil alone treatment (23.85 mg kg^{-1}).

Irrespective of treatments, the higher NH_4-N content was registered during 0th month of incubation (53.39 mg kg^{-1}). As the incubation period progressed, the NH_4-N declined sharply at 3 months of incubation and thereafter showed an increasing trend upto 9 months of incubation. After 9 months and till the end of incubation (15 MAI), a decreasing trend was seen. The interaction of incubation period with treatments further revealed that at all stages except 0th MAI, the lowest NH_4-N was registered in the control. Almost in all the treatments, the period of incubation had significant effect on the NH_4-N content.

Among the nitrogen fractions, the THyN fraction had a positive relationship with NH_4-N (0.323^{**}), whereas the NO_3-N had negative relationship (-0.252^{**}). With respect to the carbon fractions, NH_4-N had positive relationship with HWSC (0.303^{**}), POXC (0.396^{**}), organic carbon (0.317^{**}), total carbon (0.517^{**}) and negative relationship with MBC (-0.328^{**}) (Table 10).

4.4.2.1.2. Nitrate nitrogen (NO_3-N)

The results of statistical scrutiny of NO_3-N fraction in the incubation experiment is presented in the Table 19. It was seen that the NO_3-N fraction significantly increased from 224.3 mg kg^{-1} from the start of experiment to 435.2 mg kg^{-1} at 12 months of incubation and then decreased to 403.7 mg kg^{-1} at 15 MAI. However, it was much higher than the content at initial experimental phase.

Among the treatments tried, soil test based POP + biochar (424.6 mg kg^{-1}) and soil test based POP (420.9 mg kg^{-1}) registered higher values, which were comparable with each other. This was followed by the sole application of biochar at 10 t ha^{-1} (381.0 mg kg^{-1}). As expected, the lowest NO_3-N was associated with the control (291.8 mg kg^{-1}). All the other treatments varied only marginally among themselves.

The interaction of incubation period with treatments further revealed that except 3rd month of incubation, in all other stages, the lowest NO_3-N was observed in control. Additionally, it was also noticed that with an increase in levels of biochar, the NO_3-N fraction increased, but the difference between biochar levels 5 t ha^{-1} and 7.5 t ha^{-1} was only marginal.

The simple correlation studies revealed the positive and significant relationship of NO_3-N with THyN (0.262^{**}), AAN (0.685^{**}), $KMnO_4$-N (0.644^{**}) and MBC (0.423^{**}) and a negative relationship with HWSC (-0.569^{**}), POXC (-0.246^{**}) and NH_4-N (-0.252^{**}) (Table 10).

Table 18. Changes in the NH_4- N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	47.07	16.87	15.85	30.88	21.70	10.72	**23.85**
FYM 10 t ha^{-1}	48.53	18.67	22.90	49.30	24.24	12.25	**29.32**
Biochar 5 t ha^{-1}	48.53	19.33	26.97	51.11	23.64	11.18	**30.13**
Biochar 7.5 t ha^{-1}	42.93	18.73	28.53	50.13	25.41	11.93	**29.61**
Biochar 10 t ha^{-1}	46.67	18.67	21.50	48.53	22.67	12.07	**28.35**
Soil test based POP + biochar 10 t ha^{-1}	69.07	19.07	23.33	52.05	23.91	13.49	**33.49**
Soil test based POP	70.93	20.53	21.30	51.19	23.77	13.03	**33.46**
Stage (S) mean	**53.39**	**18.84**	**22.91**	**47.60**	**23.62**	**12.10**	
	S	**T**	**T x S**				
CD (0.05)	1.33	1.44	3.52				

Table 19. Changes in the NO_3- N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	203.1	297.3	336.4	316.2	296.2	301.3	**291.8**
FYM 10 t ha^{-1}	226.0	346.8	423.7	419.9	350.1	384.6	**358.5**
Biochar 5 t ha^{-1}	213.3	306.0	352.2	410.6	362.8	414.2	**343.2**
Biochar 7.5 t ha^{-1}	207.9	305.5	389.4	388.7	442.9	346.7	**346.9**
Biochar 10 t ha^{-1}	231.5	273.9	435.3	487.6	479.3	378.7	**381.0**
Soil test based POP + biochar 10 t ha^{-1}	235.3	308.7	488.2	498.8	557.7	458.8	**424.6**
Soil test based POP	253.1	316.6	405.2	452.2	557.1	541.5	**420.9**
Stage (S) mean	**224.3**	**307.8**	**404.3**	**424.9**	**435.2**	**403.7**	
	S	**T**	**T x S**				
CD (0.05)	19.0	20.5	50.3				

The rate of release of NO_3-N during the incubation period was computed by using simple regression (Table 20). In all the treatments, the variation in NO_3-N content was significantly explained by the duration of incubation. Though an increase was noticed in all the treatments, it was highest in soil test based POP followed soil test based POP + biochar (0.702 and 0.595 mg kg^{-1} day^{-1}, respectively).

The rate of increase (0.148 mg kg^{-1} day^{-1}) observed was lower in the case of soil alone treatment. It was also noticed that, the release rate of 0.446 mg kg^{-1} day^{-1}, in the biochar (10 t ha^{-1}) alone treatment got enhanced to 0.595 mg kg^{-1} day^{-1}, when soil test based POP was combined with biochar application. Similarly, when the FYM alone was applied, the rate of release was only 0.254 mg kg^{-1} day^{-1}, which further enhanced to 0.702 mg kg^{-1} day^{-1}, along with soil test based POP.

Table 20. Simple regression analysis between NO_3- N (Y) and days of incubation (X)

Treatments	R^2	a (intercept)	Rate of change (mg kg^{-1} day^{-1})
Control	0.251^{*}	258.4	0.148
FYM 10 t ha^{-1}	0.333^{*}	301.5	0.254
Biochar 5 t ha^{-1}	0.682^{**}	255.1	0.392
Biochar 7.5 t ha^{-1}	0.445^{**}	267.9	0.351
Biochar 10 t ha^{-1}	0.452^{**}	280.7	0.446
Soil test based POP + biochar 10 t ha^{-1}	0.599^{**}	290.7	0.595
Soil test based POP	0.903^{**}	263.1	0.702

4.4.2.2. Organic nitrogen fractions

4.4.2.2.1. Total hydrolysable nitrogen (THyN)

The THyN fraction as influenced by different treatments and period of incubation is presented in Table 21. Higher values of THyN was noticed in soil test based POP (1499 mg kg^{-1}) and soil test based POP + biochar (1477 mg kg^{-1}), which were comparable. The lowest THyN was registered in control (1335 mg kg^{-1}). There were only marginal differences among the other treatments. With advancement in the incubation period, the THyN increased progressively and reached its maximum (1575 mg kg^{-1}) at 6 months of incubation. Thereafter a decreasing trend was noticed and it was lowest at 15 months of incubation (1215 mg kg^{-1}). The variation in THyN content among different stages were significant.

The interaction of incubation period with treatment was significant. At all stages of incubation, the lowest THyN value was recorded in the soil alone treatment. With respect to the higher values, the effect was shared by two treatments *viz.* soil test based POP and soil test based POP + biochar.

The THyN was positively correlated with the carbon fractions *viz.* WSC (0.456**), POXC (0.417**), MBC (0.412**) and organic carbon (0.540**). Among the nitrogen fractions, a positive relationship existed with NH_4-N (0.323**), NO_3-N (0.262**) and AAN (0.440**) (Table 10).

4.4.2.2.2. Amino acid nitrogen (AAN)

The AAN fraction of soil as affected by different treatments and incubation period is presented in Table 22. The AAN fraction was found to be highest in the treatment soil test based POP (514 mg kg^{-1}), followed by soil test based POP + biochar (508 mg kg^{-1}), which were on par with each other. As could be expected, the lowest AAN content was registered in the control (322 mg kg^{-1}). The effect of other treatments on AAN content was only marginal.

The concentration of AAN was found to increase progressively from 0th month (304 mg kg^{-1}) to 12 months of incubation (556 mg kg^{-1}) and showed a sharp decline during 15 months of incubation (440 mg kg^{-1}). The increase was only marginal during the 9 and 12 months of incubation.

The interaction effect further displayed that the AAN content was lowest in the soil alone treatment, at all stages of incubation. Although applying biochar at 10 t ha^{-1} and soil test based POP registered higher AAN during 0 and 3 months of incubation, in all other stages it was the treatment soil test based POP + biochar which registered higher values.

The simple correlation analysis showed that the AAN was positively related to MBC (0.351**), NO_3-N (0.685**), THyN (0.440**) and $KMnO_4$-N (0.495**) and negatively correlated to HWSC (-0.519**) and POXC (-0.241**) (Table 10).

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Table 21. Changes in the total hydrolysable N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	1288	1344	1456	1428	1372	1120	**1335**
FYM 10 t ha^{-1}	1400	1372	1564	1502	1512	1176	**1421**
Biochar 5 t ha^{-1}	1344	1344	1624	1500	1414	1204	**1405**
Biochar 7.5 t ha^{-1}	1372	1400	1568	1540	1484	1204	**1428**
Biochar 10 t ha^{-1}	1316	1460	1624	1456	1402	1232	**1415**
Soil test based POP + biochar 10 t ha^{-1}	1456	1484	1568	1540	1512	1304	**1477**
Soil test based POP	1484	1540	1624	1596	1484	1264	**1499**
Stage (S) mean	**1380**	**1421**	**1575**	**1509**	**1454**	**1215**	
	S	**T**	**T x S**				
CD (0.05)	39	42	103				

Table 22. Changes in the amino acid N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	289	266	334	259	395	386	**322**
FYM 10 t ha^{-1}	322	294	451	544	601	398	**435**
Biochar 5 t ha^{-1}	329	285	487	548	577	442	**445**
Biochar 7.5 t ha^{-1}	289	329	495	600	604	470	**465**
Biochar 10 t ha^{-1}	292	371	469	595	512	462	**450**
Soil test based POP + biochar 10 t ha^{-1}	297	539	515	623	624	485	**514**
Soil test based POP	311	637	460	623	581	437	**508**
Stage (S) mean	**304**	**388**	**458**	**541**	**556**	**440**	
	S	**T**	**T x S**				
CD (0.05)	19	20	49				

4.4.2.3. $KMnO_4$-N (Available N)

The $KMnO_4$-N content of soil as influenced by the treatments and days of incubation is presented in Table 23. The treatments had shown significant changes not only among themselves, but also with the progression of incubation period. The $KMnO_4$-N content was found to increase with the advancement of incubation period. On an average, the $KMnO_4$-N content at the start of experiment was 116.1 mg kg^{-1}, which increased to 144.9 mg kg^{-1} at the end of incubation. However, the difference between 0^{th} and 3^{rd} month of incubation was only marginal.

Among the different treatments, the highest $KMnO_4$-N content was noticed in soil test based POP + biochar (147.3 mg kg^{-1}), followed by soil test based POP and the difference was significant. With an increase in the levels of biochar, the $KMnO_4$-N content increased, however there were no marked difference among themselves. Significantly lower $KMnO_4$-N content was recorded in the absolute control.

The interaction effect of treatments with stages of sampling had further confirmed the superiority of the treatment soil test based POP + biochar in registering higher values, however it was on par with soil test based POP. As could be expected, at all stages of sampling, significantly lower $KMnO_4$-N content was registered in soil alone treatment. It was further seen that the changes in $KMnO_4$-N content during the incubation period was insignificant in soil alone treatment. In rest of the treatments, though the increase was not substantial during the initial phases of incubation, towards the end of incubation the increase was significant with treatments.

From the simple correlation studies, it was seen that the $KMnO_4$-N content had positive relationship with different N fractions *viz.* NO_3-N (0.644^{**}) and AAN (0.495^{**}) and C fractions *viz.* MBC (0.239^{**}) and total C (0.248^{**}). It was also found to be negatively correlated with WSC (-0.490^{**}), HWSC (-0.180^{*}) and POXC (-0.198^{*}) (Table 10).

The rate of release of $KMnO_4$-N was quantified by simple regression analysis, which revealed that in all the treatments, the change in $KMnO_4$-N content could be attributed to the number of days of incubation (Table 24).

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Table 23. Changes in the $KMnO_4$-N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	97.07	98.93	104.5	105.2	107.2	105.7	**103.1**
FYM 10 t ha^{-1}	109.3	112.0	114.1	118.1	122.6	130.5	**117.8**
Biochar 5 t ha^{-1}	105.6	115.7	117.3	121.5	129.5	141.6	**121.9**
Biochar 7.5 t ha^{-1}	112.0	113.2	118.0	122.3	131.5	145.1	**123.7**
Biochar 10 t ha^{-1}	115.7	111.6	121.2	124.3	128.8	139.3	**123.5**
Soil test based POP + biochar 10 t ha^{-1}	138.5	124.3	134.7	144.4	161.3	180.5	**147.3**
Soil test based POP	134.8	127.8	129.2	141.6	155.0	171.8	**143.4**
Stage (S) mean	**116.1**	**114.8**	**119.9**	**125.3**	**133.7**	**144.9**	
	S	**T**	**T x S**				
CD (0.05)	2.3	2.5	6.1				

Table 24. Simple regression analysis between $KMnO_4$- N (Y) and days of incubation (X)

Treatments	R^2	a (intercept)	Rate of change (mg kg^{-1} day^{-1})
Control	0.638^{**}	98.20	0.022
FYM 10 t ha^{-1}	0.773^{**}	107.7	0.045
Biochar 5 t ha^{-1}	0.877^{**}	105.8	0.072
Biochar 7.5 t ha^{-1}	0.838^{**}	107.6	0.071
Biochar 10 t ha^{-1}	0.779^{**}	111.2	0.055
Soil test based POP + biochar 10 t ha^{-1}	0.732^{**}	123.7	0.105
Soil test based POP	0.733^{**}	123.4	0.089

The rate of release was found to be maximum in soil test based POP + biochar (0.105 mg kg^{-1} day^{-1}), followed by soil test based POP (0.089 mg kg^{-1} day^{-1}). The rate of release was lowest in soil alone treatment (0.022 mg kg^{-1} day^{-1}). While comparing the sole application of biochar with combined application of biochar + NPK, it was noticed that the rate of release of 0.055 mg kg^{-1} day^{-1} in the biochar (10 t ha^{-1}) alone treatment was enhanced to 0.105 mg kg^{-1} day^{-1}, when soil test based NPK application was combined with biochar. Similarly, when the FYM alone was applied, the rate of release was only 0.045 mg kg^{-1} day^{-1}, which was enhanced to 0.089 mg kg^{-1} day^{-1}, when it was applied with soil test based NPK.

4.4.2.4. Total nitrogen

The results of the total nitrogen content as influenced by the different treatments and days of incubation is presented in Table 25. The total N content showed a decreasing trend with the advancement of incubation, with the values being comparable with each other. The highest total N content was registered in the treatment, soil test based POP + biochar (2149 mg kg^{-1}), followed by soil test based POP (2134 mg kg^{-1}), biochar at 5 t ha^{-1} (2110 mg kg^{-1}) and FYM at 10 t ha^{-1} (2108 mg kg^{-1}), which were all comparable with each other. The lowest total N was recorded in soil alone treatment (2024 mg kg^{-1}).

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Table 25. Changes in the total N content (mg kg^{-1}) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	3	6	9	12	15	
Control	2030	2072	2030	1988	2008	2016	**2024**
FYM 10 t ha^{-1}	2140	2212	2128	2100	2036	2032	**2108**
Biochar 5 t ha^{-1}	2156	2184	2128	2109	2044	2036	**2110**
Biochar 7.5 t ha^{-1}	2100	2140	2100	2080	2008	2036	**2077**
Biochar 10 t ha^{-1}	2128	2100	2100	2088	2064	2068	**2091**
Soil test based POP + biochar 10 t ha^{-1}	2184	2240	2100	2100	2116	2156	**2149**
Soil test based POP	2128	2212	2100	2126	2108	2128	**2134**
Stage (S) mean	**2124**	**2166**	**2098**	**2084**	**2055**	**2067**	
	S	**T**	**T x S**				
CD (0.05)	51	55	135				

The interaction effect revealed in addition that, at all the stages of incubation, the lowest total N was associated with control. No definite trend could be identified among the different treatments within particular stage of incubation.

The simple correlation studies showed that among nitrogen fractions, the total N was positively correlated only with THyN (0.197^{*}). In respect of carbon fractions, total N exhibited a positive relationship with WSC (0.194^{*}), HWSC (0.292^{**}), POXC (0.512^{**}), organic carbon (0.525^{**}) and total carbon (0.331^{**}) (Table 10).

4.4.3. Path analysis

The direct and indirect effects of NO_3-N and AAN on available nitrogen as indicated by path coefficients are given in Table 26. The direct effect of NO_3-N on available nitrogen was very high and positive (0.574) and the indirect effect was quite negligible. With respect to the AAN, direct effect was low (0.102), whereas the indirect effect of AAN through NO_3-N was positive and very high (0.393).

Path coefficients specifying the direct as well as the indirect effects of carbon fractions *viz.* WSC, HWSC, POXC, MBC and TOC on available nitrogen is presented in Table 27. The direct effect of MBC (0.40) and TOC (0.338) on available nitrogen was very high and positive, whereas the direct effect of WSC was negative, but very high (-0.634). The direct effect of HWSC was low and negative (-0.140) and the direct effect of POXC was negligible. The indirect effect of POXC through WSC though high, was negative (-0.302). All other indirect effects were negligible.

Path coefficient of different fractions of carbon indicating the direct and indirect effects on organic carbon is given in the Table 28. The direct effect of POXC and MBC on organic carbon was very high (0.684) and moderate (0.255), respectively. The indirect effect of WSC (0.326) and HWSC (0.323) through POXC was high and positive. All the other effects were negligible.

Path coefficients explaining the direct as well as the indirect effects of different fractions of nitrogen on organic carbon is presented in Table 29. The direct effect of THyN (0.418) and total nitrogen (0.424) was very high and positive, whereas the effect of NH_4-N was low (0.118). The indirect effects were on the whole negligible.

Table 26. Path coefficients of different fractions of nitrogen to available N

	NO$_3$-N	AAN	Correlation coefficient
NO$_3$-N	**0.574**	0.070	0.644
AAN	0.393	**0.102**	0.495

Table 27. Path coefficients of different fractions of carbon to available N

	WSC	HWSC	POXC	MBC	Total C	Correlation coefficient
WSC	**-0.634**	-0.018	0.011	0.119	0.033	-0.490
HWSC	-0.081	**-0.140**	0.011	-0.072	0.101	-0.180
POXC	-0.302	-0.066	**0.023**	0.003	0.144	-0.198
MBC	-0.188	0.025	0.002	**0.400**	0.002	0.239
Total C	-0.061	-0.042	0.010	0.003	**0.338**	0.248

Table 28. Path coefficients of different fractions of carbon to organic carbon

	WSC	HWSC	POXC	MBC	Correlation coefficient
WSC	**0.010**	0.008	0.326	0.075	0.419
HWSC	0.001	**0.062**	0.323	-0.046	0.340
POXC	0.005	0.029	**0.684**	0.002	0.720
MBC	0.003	-0.011	0.005	**0.255**	0.252

Table 29. Path coefficients of different fractions of nitrogen to organic carbon

	NH$_4$-N	THyN	Total N	Correlation coefficient
NH$_4$-N	**0.118**	0.135	0.064	0.317
THyN	0.038	**0.418**	0.084	0.540
Total N	0.018	0.082	**0.424**	0.525

(WSC – Water soluble C, HWSC – Hot water soluble C, POXC – Permanganate oxidizable C, MBC – Microbial biomass C, THyN – Total hydrolysable N, AAN – Amino acid N)

4.4.4. Maximum water holding capacity (MWHC)

The MWHC of soil was found to decrease significantly with the progression of incubation (Table 30). On an average, the MWHC at the beginning of experiment was 37.14 per cent, which decreased to 33.12 per cent towards the end.

Table 30. Changes in the maximum water holding capacity (%) at different stages of incubation

Treatments	Incubation period (months)						Treatment (T) mean
	0	**3**	**6**	**9**	**12**	**15**	
Control	34.59	34.24	34.18	33.19	32.20	31.47	**33.31**
FYM 10 t ha^{-1}	36.73	36.13	35.84	34.77	33.90	33.16	**35.09**
Biochar 5 t ha^{-1}	37.66	36.80	34.95	33.88	33.08	32.80	**34.86**
Biochar 7.5 t ha^{-1}	37.89	36.07	35.45	34.91	33.99	33.18	**35.25**
Biochar 10 t ha^{-1}	37.85	37.58	36.70	35.49	34.55	33.93	**36.02**
Soil test based POP + biochar 10 t ha^{-1}	38.22	37.35	35.11	35.21	34.48	34.10	**35.75**
Soil test based POP	37.02	35.93	35.44	35.07	34.32	33.20	**35.16**
Stage (S) mean	**37.14**	**36.30**	**35.38**	**34.65**	**33.79**	**33.12**	
	S	**T**	**T x S**				
CD (0.05)	0.44	0.48	1.16				

On comparing it was seen that, the biochar at 10 t ha^{-1} had recorded the highest MWHC (36.02 %), followed by soil test based POP + biochar (35.75 %), which were on par. Significantly lower MWHC was registered in soil alone treatment (33.31 %). In rest of the treatments, the differences were only marginal. MWHC in the rest of the treatments had registered values ranging from 34.86 to 35.25 per cent, with no marked difference among them. With an increase in rate of biochar application, the MWHC also increased, but the difference was only comparable between 5 and 7.5 t ha^{-1} biochar.

The interaction effect further substantiated the superiority of biochar at 10 t ha^{-1} and soil test based POP + biochar in registering higher MWHC at all stages of incubation. Similarly, the lower MWHC was recorded in soil alone treatment at all stages of incubation.

4.4.5. Fraction of organic matter

4.4.5.1. Fulvic acid

Statistical analysis of fulvic acid content of soil under various treatments are shown in Table 31. The fulvic acid content of soil ranged from 6.430 to 7.900 per cent. Among the various treatments, it was the highest in the treatment biochar at 10 t ha^{-1} (7.900 %). However, it was on par with all other treatments, except control (6.433 %). Significantly lower per cent of fulvic acid was recorded in control. With an increase in biochar application rate, the fulvic acid content also increased, although the differences were only marginal.

4.4.5.2. Humic acid

Statistical analysis of the data specified that humic acid content was significantly influenced by the treatments (Table 31). Significantly the highest humic acid content of 6.067 per cent was recorded in the treatment biochar at 10 t ha^{-1} which was followed by the application of soil test based POP + biochar (5.300 %). The differences were significant not only among themselves, but also from rest of the treatments. The effects of biochar at 7.5 t ha^{-1} (4.433 %) and soil test based POP (4.367 %) were comparable with each other.

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Lowest amount of humic acid was registered in the soil alone treatment (3.367 %), which was on par with FYM at 10 t ha^{-1} (3.700 %) and biochar at 5 t ha^{-1} (3.700 %). It was further noticed that, an increase in the rate of biochar application brought about a significant increase in humic acid content.

Table 31. Effect of biochar application on fraction of organic matter after incubation

Treatments	**Fulvic acid**	**Humic acid**
	%	
Control	6.433	3.367
FYM 10 t ha^{-1}	7.433	3.700
Biochar 5 t ha^{-1}	7.533	3.700
Biochar 7.5 t ha^{-1}	7.767	4.433
Biochar 10 t ha^{-1}	7.900	6.067
Soil test based POP + biochar 10 t ha^{-1}	7.833	5.300
Soil test based POP	7.817	4.367
CD (0.05)	0.557	0.410

4.5. Field experiment

Two field experiments were carried out successively under natural environment, wherein the first season was with Chinese potato as a test crop to study the direct effect of biochar and the second season with cowpea as the test crop to study the residual effect of biochar. Soil and plant samples were collected at the harvest stage to study the effect of treatments on soil properties; growth, yield and quality of crop and also on its nutrient uptake. The results were statistically scrutinized and presented in this section.

4.5.1. Direct and residual effect of biochar on soil properties

4.5.1.1. Soil reaction

Statistical scrutiny of the data revealed that there was significant difference among the treatments with respect to soil pH (Table 32). The initial pH of the experimental soil was 5.24. Maximum pH of 5.95 was observed in the treatment biochar 10 t ha^{-1} and was superior to all other treatments. In the succeeding crop also the higher value was associated with the same treatment. However, it was on par with the application of soil test based POP + biochar (5.98) and biochar 7.5 t ha^{-1} (5.96). Irrespective of the treatments, soil pH increased significantly in the succeeding crop. Increase in pH with an increase in levels of biochar was also observed. In both the experiments, the lowest pH was recorded in control.

The inter relationship of soil properties had shown that the pH was positively correlated with organic carbon, CEC, dehydrogenase activity, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Cu and hot water soluble B during the main crop (Table 33) and with organic carbon, CEC, dehydrogenase activity, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B in the succeeding crop. However, it was negatively correlated with HCl-Mn (Table 34).

Table 32. Effect of biochar application on pH of post-harvest soil

Treatments	**First season**	**Second season**	**Treatment Mean (T)**
Control	5.21	5.43	**5.32**
FYM 10 t ha^{-1}	5.36	5.86	**5.61**
Biochar 5 t ha^{-1}	5.49	5.89	**5.69**
Biochar 7.5 t ha^{-1}	5.65	5.96	**5.80**
Biochar 10 t ha^{-1}	5.86	6.04	**5.95**
Soil test based POP + biochar 10 t ha^{-1}	5.71	5.98	**5.84**
Soil test based POP	5.27	5.67	**5.47**
Season (S) mean	**5.51**	**5.83**	
	S	**T**	**T x S**
CD (0.05)	0.05	0.09	0.12

4.5.1.2. Electrical conductivity (EC)

The EC values of post-harvest soil as influenced by different treatments is presented in Table 35. The highest EC values was registered in the treatment soil test based POP + biochar (0.084 dS m^{-1}), followed by soil test based POP application (0.068 dS m^{-1}) and the difference was significant. The effect of all other treatments were on par. In the succeeding crop, the effect of different treatments on EC was comparable. Irrespective of the treatments, the higher EC values were recorded in the succeeding crop.

Table 33. Correlation analysis among the post-harvest soil properties of Chinese potato (n = 21)

	pH	EC	OC	CEC	MBC	DHY	N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH	1.000																
EC	0.046^{NS}	1.000															
OC	0.835^{**}	0.110^{NS}	1.000														
CEC	0.870^{**}	0.296^{NS}	0.820^{**}	1.000													
MBC	0.388^{NS}	0.197^{NS}	0.721^{**}	0.572^{**}	1.000												
DHY	0.857^{**}	0.392^{NS}	0.873^{**}	0.873^{**}	0.616^{**}	1.000											
N	0.297^{NS}	0.488^{*}	0.514^{*}	0.463^{*}	0.507^{*}	0.606^{**}	1.000										
P	0.071^{NS}	0.834^{**}	0.132^{NS}	0.363^{NS}	0.417^{NS}	0.375^{NS}	0.429^{NS}	1.000									
K	0.953^{**}	0.006^{NS}	0.842^{**}	0.833^{**}	0.402^{NS}	0.800^{**}	0.278^{NS}	0.029^{NS}	1.000								
Ca	0.489^{*}	0.541^{*}	0.381^{NS}	0.680^{**}	0.342^{NS}	0.546^{*}	0.430^{NS}	0.619^{**}	0.294^{NS}	1.000							
Mg	0.481^{*}	0.732^{**}	0.336^{NS}	0.450^{*}	0.507^{*}	0.497^{*}	0.595^{**}	0.796^{**}	0.065^{NS}	0.764^{**}	1.000						
S	-0.182^{NS}	0.672^{**}	-0.104^{NS}	0.130^{NS}	0.242^{NS}	0.071^{NS}	0.077^{NS}	0.776^{**}	-0.180^{NS}	0.274^{NS}	0.477^{*}	1.000					
Fe	0.296^{NS}	0.171^{NS}	0.237^{NS}	0.329^{NS}	0.095^{NS}	0.200^{NS}	0.030^{NS}	0.118^{NS}	0.170^{NS}	0.478^{*}	0.320^{NS}	0.015^{NS}	1.000				
Mn	0.295^{NS}	0.098^{NS}	0.236^{NS}	0.327^{NS}	0.278^{NS}	0.211^{NS}	0.058^{NS}	0.314^{NS}	0.215^{NS}	0.520^{*}	0.381^{NS}	0.094^{NS}	0.502^{*}	1.000			
Zn	0.311^{NS}	0.529^{*}	0.394^{NS}	0.380^{NS}	0.442^{*}	0.535^{*}	0.526^{*}	0.610^{**}	0.188^{NS}	0.533^{*}	0.666^{**}	0.391^{NS}	0.106^{NS}	0.227^{NS}	1.000		
Cu	0.584^{**}	-0.390^{NS}	0.557^{**}	0.401^{NS}	0.363^{NS}	0.464^{*}	0.273^{NS}	-0.270^{NS}	0.598^{**}	0.046^{NS}	-0.062^{NS}	-0.521^{*}	0.236^{NS}	0.349^{NS}	-0.010^{NS}	1.000	
B	0.738^{**}	-0.437^{*}	0.625^{**}	0.548^{*}	0.359^{NS}	0.481^{*}	0.043^{NS}	-0.251^{NS}	0.697^{**}	0.190^{NS}	-0.096^{NS}	-0.469^{*}	0.213^{NS}	0.293^{NS}	0.015^{NS}	0.714^{**}	1.000

(** - Significant at 0.01 level, * - Significant at 0.05 level) (MBC – Microbial biomass carbon, DHY – Dehydrogenase activity)

Table 34. Correlation analysis among the post-harvest soil properties of cowpea (n = 21)

	PH	EC	OC	CEC	MBC	DHY	N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH	1.000																
EC	-0.226^{NS}	1.000															
OC	0.830**	-0.073^{NS}	1.000														
CEC	0.773**	-0.259^{NS}	0.785**	1.000													
MBC	0.321^{NS}	0.345^{NS}	0.599**	0.344^{NS}	1.000												
DHY	0.440*	0.244^{NS}	0.554**	0.606**	0.399^{NS}	1.000											
N	0.273^{NS}	0.370^{NS}	0.554**	0.273^{NS}	0.658**	0.639**	1.000										
P	0.348^{NS}	0.132^{NS}	0.473*	0.529*	0.413^{NS}	0.600**	0.527*	1.000									
K	0.810**	-0.423^{NS}	0.582**	0.743**	0.166^{NS}	0.104^{NS}	-0.094^{NS}	0.165^{NS}	1.000								
Ca	0.709**	-0.404^{NS}	0.727**	0.757**	0.301^{NS}	0.168^{NS}	0.113^{NS}	0.305^{NS}	0.798**	1.000							
Mg	0.678**	-0.445*	0.591**	0.479*	0.168^{NS}	0.008^{NS}	0.174^{NS}	0.321^{NS}	0.614**	0.668**	1.000						
S	0.096^{NS}	0.661**	0.407^{NS}	0.080^{NS}	0.584**	0.548*	0.819**	0.319^{NS}	-0.315^{NS}	-0.174^{NS}	-0.106^{NS}	1.000					
Fe	0.175^{NS}	-0.020^{NS}	0.279^{NS}	0.413^{NS}	0.208^{NS}	0.447*	0.244^{NS}	0.141^{NS}	0.192^{NS}	0.153^{NS}	-0.094^{NS}	0.109^{NS}	1.000				
Mn	-0.724**	0.189^{NS}	-0.578**	-0.629**	-0.431^{NS}	-0.253^{NS}	-0.166^{NS}	-0.089^{NS}	-0.817**	-0.613**	-0.425^{NS}	0.014^{NS}	-0.335^{NS}	1.000			
Zn	0.620**	0.061^{NS}	0.573**	0.718**	0.390^{NS}	0.725**	0.422^{NS}	0.782**	0.380^{NS}	0.300^{NS}	0.262^{NS}	0.303^{NS}	0.155^{NS}	-0.297^{NS}	1.000		
Cu	0.537*	-0.444*	0.499*	0.591**	0.232^{NS}	0.127^{NS}	0.023^{NS}	0.424^{NS}	0.761**	0.703**	0.591**	-0.312^{NS}	0.220^{NS}	-0.584**	0.299^{NS}	1.000	
B	0.692**	-0.277^{NS}	0.713**	0.767**	0.329^{NS}	0.464*	0.387^{NS}	0.675**	0.638**	0.693**	0.787**	0.096^{NS}	0.202^{NS}	-0.525*	0.595**	0.696**	1.000

(** - Significant at 0.01 level, * - Significant at 0.05 level) (MBC – Microbial biomass carbon, DHY – Dehydrogenase activity)

Table 35. Effect of biochar application on electrical conductivity (dS m^{-1}) of post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	0.054	0.061	**0.058**
FYM 10 t ha^{-1}	0.058	0.070	**0.064**
Biochar 5 t ha^{-1}	0.048	0.066	**0.057**
Biochar 7.5 t ha^{-1}	0.050	0.058	**0.054**
Biochar 10 t ha^{-1}	0.050	0.058	**0.054**
Soil test based POP + biochar 10 t ha^{-1}	0.084	0.066	**0.075**
Soil test based POP	0.068	0.070	**0.069**
Season (S) mean	**0.059**	**0.064**	
	S	T	T x S
CD (0.05)	0.002	0.004	0.006

4.5.1.3. Organic carbon

Application of different levels of biochar significantly influenced the organic carbon content of post-harvest soil (Table 36). The initial organic carbon content of the experimental soil was 1.55 per cent and an increase in the value owing to the application of treatments was observed. In both the main and succeeding crop, application of biochar 10 t ha^{-1} either alone or in combination with soil test based POP showed a superior effect by registering significantly higher organic carbon values. As could be expected, significantly the lowest organic carbon was recorded in the absolute control, in both experiments (1.581 and 1.573 %, respectively). With an increase in levels of biochar, significant increase in organic carbon was noticed and the trend was similar in the case of residual effect also.

The simple correlation studies among the soil properties had shown that the organic carbon was positively correlated with pH, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, NH_4OAc-K, HCl-Cu and hot water soluble B during the main crop (Table 33) and with Bray-P, NH_4OAc-Ca, NH_4OAc-Mg and HCl-Zn during the succeeding crop. Negative correlation was obtained between organic carbon and HCl-Mn (Table 34).

Table 36. Effect of biochar application on organic carbon content (%) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	1.581	1.573	**1.577**
FYM 10 t ha^{-1}	1.696	1.660	**1.678**
Biochar 5 t ha^{-1}	1.790	1.771	**1.780**
Biochar 7.5 t ha^{-1}	1.828	1.824	**1.826**
Biochar 10 t ha^{-1}	1.933	1.942	**1.938**
Soil test based POP + biochar 10 t ha^{-1}	1.925	1.913	**1.919**
Soil test based POP	1.695	1.686	**1.691**
Season (S) mean	**1.778**	**1.767**	
	S	**T**	**T x S**
CD (0.05)	0.014	0.026	0.037

4.5.1.4. Exchangeable acidity

The effect of different treatments on the exchangeable acidity of soils revealed that, during the main crop exchangeable acidity was found to be the highest with the application of soil test based POP (0.093 meq 100g^{-1}), followed by control (0.087 meq 100g^{-1}), which was comparable with each other. In the succeeding crop, the effect of different treatments was only comparable (Table 37).

Table 37. Effect of biochar application on exchangeable acidity (meq 100g^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	0.087	0.070	**0.078**
FYM 10 t ha^{-1}	0.057	0.057	**0.057**
Biochar 5 t ha^{-1}	0.077	0.047	**0.062**
Biochar 7.5 t ha^{-1}	0.050	0.045	**0.048**
Biochar 10 t ha^{-1}	0.040	0.043	**0.042**
Soil test based POP + biochar 10 t ha^{-1}	0.050	0.053	**0.052**
Soil test based POP	0.093	0.050	**0.072**
Season (S) mean	**0.065**	**0.052**	
	S	**T**	**T x S**
CD (0.05)	0.005	0.010	0.014

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In both experiments, the lowest exchangeable acidity was registered by biochar 10 t ha^{-1} (0.040 and 0.043 meq 100g^{-1}, respectively), but not significantly from other treatments. With an increase in the biochar application rate, exchangeable acidity decreased, however the decrease was only marginal.

4.5.1.5. $KMnO_4$-N

In the post-harvest soil of main crop, the $KMnO_4$-Ncontent of soil was found to be higher in plots which received soil test based POP + biochar (217.7 kg ha^{-1}) and biochar 5 t ha^{-1} (212.6 kg ha^{-1}), which were on par (Table 38). In the succeeding crop also soil test based POP + biochar application recorded higher value (194.1 kg ha^{-1}), but it was on par with soil test based POP (190.8 kg ha^{-1}) and biochar 5 t ha^{-1} (190.7 kg ha^{-1}). In both experiments, the lowest value was recorded in the control plots. Further it was seen that the decline in the $KMnO_4$-N content after the second experiment was significant than that of the first crop.

The inter relationship of soil properties had shown that $KMnO_4$-N content of soil was positively related with EC, organic carbon, CEC, MBC, NH_4OAc-Mg and HCl-Zn (Table 33 and 34).

Table 38. Effect of biochar application on $KMnO_4$- N content (kg ha^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	194.7	174.0	**184.4**
FYM 10 t ha^{-1}	210.0	186.4	**198.2**
Biochar 5 t ha^{-1}	212.6	190.7	**201.6**
Biochar 7.5 t ha^{-1}	200.6	183.8	**192.2**
Biochar 10 t ha^{-1}	204.0	176.8	**190.4**
Soil test based POP + biochar 10 t ha^{-1}	217.7	194.1	**205.9**
Soil test based POP	203.2	190.8	**197.0**
Season (S) mean	**206.1**	**185.2**	
	S	**T**	**T x S**
CD (0.05)	2.8	5.2	7.3

4.5.1.6. Bray- P

The Bray-P content in the post-harvest soil varied among the treatments (Table 39). There was an increase in Bray-P status when compared to its initial value (27.08 kg ha^{-1}) and the values were found to be significantly higher in the first experiment. After the first experiment, the Bray-P content of soil was found to be higher in the plots which received soil test based POP + biochar (74.79 kg ha^{-1}), followed by soil test based POP (70.10 kg ha^{-1}) and FYM 10 t ha^{-1} (61.34 kg ha^{-1}) which were on par with each other but superior to rest of the treatments. Similarly, in the succeeding crop, the highest Bray-P content was recorded in soil test based POP + biochar (52.23 kg ha^{-1}), biochar 10 t ha^{-1} (50.78 kg ha^{-1}), soil test based POP (49.91 kg ha^{-1}) and FYM 10 t ha^{-1} (47.46 kg ha^{-1}) application which were all comparable. In both experiments, the lowest value was in control.

Table 39. Effect of biochar application on Bray-P content (kg ha^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	26.18	32.74	**29.46**
FYM 10 t ha^{-1}	61.34	47.46	**54.40**
Biochar 5 t ha^{-1}	27.04	36.14	**31.59**
Biochar 7.5 t ha^{-1}	38.92	50.78	**44.85**
Biochar 10 t ha^{-1}	42.93	42.15	**42.54**
Soil test based POP + biochar 10 t ha^{-1}	74.79	52.23	**63.51**
Soil test based POP	70.10	49.61	**59.86**
Season (S) mean	**48.76**	**44.44**	
	S	T	T x S
CD (0.05)	3.37	6.31	8.92

4.5.1.7. NH_4OAc-K

Perusal of data in the Table 40 showed that in all the treatments NH_4OAc-K was maximum in the main crop. In both experiments, significantly higher NH_4OAc-K content was registered by the treatment biochar 10 t ha^{-1}. Further it can be inferred from the table that, the effect of different treatments *viz.* biochar 5 t ha^{-1}, 7.5 t ha^{-1} and 10 t ha^{-1} and soil test based POP in registering higher NH_4OAc-K was not only significant among them, but also from rest of the treatments, in both experiments.

With an increase in the levels of biochar, NH_4OAc-K content increased significantly. Although the effect of FYM 10 t ha^{-1}, soil test based POP and control on NH_4OAc-K was comparable, the lowest value was associated with control plots in both cases.

Table 40. Effect of biochar application on NH_4OAc-K content (kg ha^{-1}) in post-harvest soil

Treatments	**First season**	**Second season**	**Treatment Mean (T)**
Control	365.5	257.4	**311.4**
FYM 10 t ha^{-1}	394.2	304.5	**349.4**
Biochar 5 t ha^{-1}	536.9	375.0	**455.9**
Biochar 7.5 t ha^{-1}	589.0	425.7	**507.3**
Biochar 10 t ha^{-1}	680.9	481.9	**581.4**
Soil test based POP + biochar 10 t ha^{-1}	607.2	370.6	**488.9**
Soil test based POP	422.1	286.7	**354.4**
Season (S) mean	**513.7**	**357.4**	
	S	**T**	**T x S**
CD (0.05)	17.0	31.7	44.9

The inter relationship of soil properties had shown that NH_4OAc-K content of soil was positively related with pH, CEC, dehydrogenase activity, organic carbon, NH_4OAc-Ca, NH_4OAc-Mg, HCl- Cu and hot water soluble B (Table 33 and 34).

4.5.1.8. NH_4OAc-Ca

The results of the NH_4OAc-Ca content of post-harvest soil is presented in Table 41. In the post-harvest soil of main crop, NH_4OAc-Ca was found to be higher in the treatment soil test based POP + biochar (387.7 mg kg^{-1}), however it was on par with biochar 10 t ha^{-1}, FYM 10 t ha^{-1}, soil test based POP application. With respect to the succeeding crop, the higher values were observed in biochar 7.5 t ha^{-1}, biochar 10 t ha^{-1}, biochar 5 t ha^{-1} which were all comparable. Irrespective of the treatments, the NH_4OAc-Ca content was higher in the second experiment. In both experiments, the lowest value was associated with the control plots.

The simple correlation studies among the soil properties disclosed that the NH_4OAc-Ca was positively correlated with pH, EC, CEC, dehydrogenase activity, Bray-P, NH_4OAc-Mg, HCl-Fe, HCl-Mn and HCl-Zn during the main crop (Table 33) and with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Mg, HCl-Cu and hot water soluble B during the succeeding crop. Negative correlation was obtained between NH_4OAc-Ca and HCl-Mn (Table 34).

Table 41. Effect of biochar application on NH_4OAc-Ca content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	346.6	367.4	**357.0**
FYM 10 t ha^{-1}	376.3	389.9	**383.1**
Biochar 5 t ha^{-1}	352.0	416.6	**384.3**
Biochar 7.5 t ha^{-1}	358.8	431.2	**395.0**
Biochar 10 t ha^{-1}	377.7	426.3	**402.0**
Soil test based POP + biochar 10 t ha^{-1}	387.7	405.0	**396.4**
Soil test based POP	372.1	391.2	**381.7**
Season (S) mean	**367.3**	**404.0**	
	S	**T**	**T x S**
CD (0.05)	8.6	16.1	22.8

4.5.1.9. NH_4OAc-Mg

The NH_4OAc-Mg content of soil amended with different treatments showed changes not only among the treatments but also over the season (Table 42). During the main crop, the NH_4OAc-Mg was found to be highest in the soil test based POP + biochar (73.92 mg kg^{-1}), followed by FYM 10 t ha^{-1} (70.22 mg kg^{-1}) and soil test based POP (67.62 mg kg^{-1}) application, which were all comparable but superior to rest of the treatments.

In the post-harvest soil of succeeding crop, significantly highest NH_4OAc-Mg was recorded in biochar 7.5 t ha^{-1}. As could be expected, the control plots recorded the lowest value in both experiments. Furthermore, a gradual increase in the NH_4OAc-Mg with an increase in the levels of biochar was noticed during the main crop, whereas in succeeding crop there was no such trend.

The simple correlation studies among the soil properties had indicated that the NH_4OAc-Mg was positively correlated with pH, EC, CEC, MBC, dehydrogenase

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activity, $KMnO_4$-N, Bray-P, NH_4OAc-Ca, $CaCl_2$-S and HCl-Zn during the main crop (Table 33) and with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca, HCl-Cu and hot water soluble boron during the succeeding crop (Table 34).

Table 42. Effect of biochar application on NH_4OAc-Mg content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	50.90	79.57	**65.23**
FYM 10 t ha^{-1}	70.22	93.27	**81.74**
Biochar 5 t ha^{-1}	55.78	96.63	**76.21**
Biochar 7.5 t ha^{-1}	58.37	110.33	**84.35**
Biochar 10 t ha^{-1}	59.95	93.47	**76.71**
Soil test based POP + biochar 10 t ha^{-1}	73.92	90.77	**82.34**
Soil test based POP	67.62	86.83	**77.23**
Season (S) mean	**62.39**	**92.98**	
	S	T	T x S
CD (0.05)	2.52	4.72	6.68

4.5.1.10. $CaCl_2$-S

Data pertaining to the $CaCl_2$-S content of soil as affected by different treatments is presented in Table 43. During the main crop, $CaCl_2$-S content was found to be the highest in the soil applied with soil test based POP (10.71 mg kg^{-1}) and soil test based POP + biochar (10.31 mg kg^{-1}) which were on par with each other. The lowest $CaCl_2$-S was recorded in biochar at 5 t ha^{-1} (7.023 mg kg^{-1}).

In the succeeding crop, the higher values were associated with the treatments soil test based POP, soil test based POP + biochar, biochar 5 t ha^{-1} and FYM 10 t ha^{-1} which were all comparable, but superior to rest of the treatments. In general, the values of $CaCl_2$-S decreased after succeeding crop.

The inter relationship of soil properties had shown that the $CaCl_2$-S was positively correlated with EC, Bray-P, NH_4OAc-Mg and negatively with HCl-Cu and hot water soluble boron during the main crop (Table 33). In the crop that followed, it was found to have positive correlation with EC, MBC, dehydrogenase activity and $KMnO_4$-N (Table 34).

Table 43. Effect of biochar application on $CaCl_2$-S content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	8.267	6.194	**7.230**
FYM 10 t ha^{-1}	8.923	7.856	**8.390**
Biochar 5 t ha^{-1}	7.023	8.362	**7.693**
Biochar 7.5 t ha^{-1}	9.140	6.347	**7.743**
Biochar 10 t ha^{-1}	7.453	6.062	**6.758**
Soil test based POP + biochar 10 t ha^{-1}	10.310	8.509	**9.408**
Soil test based POP	10.710	8.552	**9.631**
Season (S) mean	**8.832**	**7.412**	
	S	**T**	**T x S**
CD (0.05)	0.465	0.871	1.231

4.5.1.11. HCl-Fe

Perusal of data in Table 44 revealed that the effect of different treatments on HCl-Fe was only comparable. However, application of biochar 10 t ha^{-1} and soil test based POP + biochar recorded numerically higher values in the main and succeeding crop, respectively. It was further noticed that the HCl-Fe content was significantly higher in the second experiment.

4.5.1.12. HCl-Mn

The data on HCl extractable Mn influenced by different treatments is presented in Table 45. In the post-harvest soil of main crop, HCl-Mn was found to be higher in the treatment biochar at 10 t ha^{-1} (44.56 mg kg^{-1}), followed by rest of the treatments which were comparable. The lowest value was observed in absolute control (35.26 mg kg^{-1}).

The trend was reverse in the case of succeeding crop, wherein the treatment absolute control and FYM 10 t ha^{-1} recorded higher HCl-Mn values, which was on par with each other, but significantly differed from rest of the treatments. Significantly the lowest amount of HCl-Mn was recorded by the treatment biochar 10 t ha^{-1} (36.55 mg kg^{-1}), which showed the highest HCl-Mn content after the main crop. It was further noticed that, except biochar 10 t ha^{-1}, in all other treatments, the HCl-Mn content increased after vegetable cowpea.

Table 44. Effect of biochar application on HCl-Fe content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	17.00	19.18	**18.09**
FYM 10 t ha^{-1}	17.33	18.02	**17.68**
Biochar 5 t ha^{-1}	16.64	19.88	**18.26**
Biochar 7.5 t ha^{-1}	17.02	19.44	**18.23**
Biochar 10 t ha^{-1}	18.64	20.02	**19.33**
Soil test based POP + biochar 10 t ha^{-1}	18.03	21.18	**19.61**
Soil test based POP	17.68	20.09	**18.89**
Season (S) mean	**17.48**	**19.69**	
	S	**T**	**T x S**
CD (0.05)	0.77	1.44	2.03

Table 45. Effect of biochar application on HCl-Mn content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	35.26	50.76	**43.01**
FYM 10 t ha^{-1}	41.06	50.26	**45.66**
Biochar 5 t ha^{-1}	36.79	41.37	**39.04**
Biochar 7.5 t ha^{-1}	36.75	42.26	**39.51**
Biochar 10 t ha^{-1}	44.56	36.55	**40.55**
Soil test based POP + biochar 10 t ha^{-1}	38.57	42.47	**40.52**
Soil test based POP	41.34	44.72	**43.03**
Season (S) mean	**39.20**	**44.06**	
	S	**T**	**T x S**
CD (0.05)	2.02	3.77	5.32

The inter relationship of soil properties disclosed that the HCl-Mn was negatively correlated with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca, HCl-Cu and hot water soluble B (Table 33 and 34).

4.5.1.13. HCl-Zn

Perusal of data in Table 46 showed that the HCl extractable Zn was maximum after the main crop, wherein the highest value of 7.207 mg kg^{-1} was

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recorded by the treatment soil test based POP + biochar, which was on par with FYM 10 t ha^{-1} (6.843 mg kg^{-1}). Control registered the lowest value of 5.193 mg kg^{-1}.

In the succeeding crop, the effect of treatments was only marginal. As could be expected, the lowest HCl-Zn was recorded in control, in both experiments. Further it was noticed that with an increase in biochar levels, the HCl-Zn increased, though only marginally.

The simple correlation studies among the soil properties had shown that the HCl-Zn was positively correlated with EC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-Ca and NH_4OAc-Mg during the main crop (Table 33) and with pH, organic carbon, CEC, dehydrogenase activity, Bray-P and hot water soluble B during the succeeding crop (Table 34).

Table 46. Effect of biochar application on HCl-Zn content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	5.193	4.943	**5.068**
FYM 10 t ha^{-1}	6.843	6.197	**6.520**
Biochar 5 t ha^{-1}	5.613	5.283	**5.448**
Biochar 7.5 t ha^{-1}	5.990	5.920	**5.955**
Biochar 10 t ha^{-1}	6.077	6.133	**6.105**
Soil test based POP + biochar 10 t ha^{-1}	7.207	6.567	**6.887**
Soil test based POP	6.090	5.933	**6.012**
Season (S) mean	**6.145**	**5.854**	
	S	**T**	**T x S**
CD (0.05)	0.276	0.517	0.731

4.5.1.14. HCl-Cu

Statistical analysis of data presented in Table 47 revealed that the HCl extractable Cu was significantly higher in the post-harvest soil of second experiment. The HCl-Cu content was highest in the treatment biochar 10 t ha^{-1} during the main crop and biochar 7.5 t ha^{-1} after the next crop, followed by rest of the treatments which were comparable with each other. The lower value was registered in control plot, in both experiments.

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The HCl extractable Cu was significantly and positively related to pH, organic carbon, dehydrogenase activity, NH_4OAc-K and negatively to $CaCl_2$-S and hot water soluble B during the main crop (Table 33). In the subsequent crop, it was found to have positive relationship with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg and hot water soluble B and negative relation with electrical conductivity and HCl-Mn (Table 34).

Table 47. Effect of biochar application on HCl-Cu content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	1.723	2.203	**1.963**
FYM 10 t ha^{-1}	1.930	2.233	**2.082**
Biochar 5 t ha^{-1}	2.047	2.350	**2.198**
Biochar 7.5 t ha^{-1}	1.913	2.557	**2.235**
Biochar 10 t ha^{-1}	2.123	2.527	**2.325**
Soil test based POP + biochar 10 t ha^{-1}	1.867	2.400	**2.133**
Soil test based POP	1.753	2.337	**2.045**
Season (S) mean	**1.908**	**2.372**	
	S	T	T x S
CD (0.05)	0.059	0.110	0.155

4.5.1.15. Hot water soluble B

The data presented in Table 48 showed that different treatments tried brought about a variation in the hot water soluble B content. During the main crop, the effect in registering higher value was shared by two treatments *viz.* biochar 10 t ha^{-1} (0.170 mg kg^{-1}) and biochar 7.5 t ha^{-1} (0.160 mg kg^{-1}). Lower value was registered in control (0.109 mg kg^{-1}) which was on par with soil test based POP + biochar (0.125 mg kg^{-1}) and soil test based POP (0.113 mg kg^{-1}) application.

In the ensuing crop, the higher value was recorded in the treatment biochar 7.5 t ha^{-1} (0.222 mg kg^{-1}), followed by the application of soil test based POP + biochar (0.191 mg kg^{-1}). Both the treatments showed significant difference not only among themselves but also from rest of the treatments. Significantly lower value was registered in absolute control (0.097 mg kg^{-1}). Further it was seen that, irrespective of treatments, the hot water soluble B increased significantly after the succeeding crop.

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The simple correlation studies among the soil properties disclosed that the hot water soluble B was significantly and positively correlated with pH, organic carbon, CEC, dehydrogenase activity, NH_4OAc-K and HCl-Cu and negatively with electrical conductivity and $CaCl_2$-S during the main crop (Table 33). During the consecutive crop, positive relationship occurred between hot water soluble B and pH, organic carbon, CEC, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn and HCl-Cu and negative with HCl-Mn (Table 34).

Table 48. Effect of biochar application on hot water soluble B content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	0.109	0.097	**0.103**
FYM 10 t ha^{-1}	0.133	0.137	**0.135**
Biochar 5 t ha^{-1}	0.135	0.147	**0.141**
Biochar 7.5 t ha^{-1}	0.160	0.222	**0.191**
Biochar 10 t ha^{-1}	0.170	0.160	**0.165**
Soil test based POP + biochar 10 t ha^{-1}	0.125	0.191	**0.158**
Soil test based POP	0.113	0.152	**0.133**
Season (S) mean	**0.135**	**0.158**	
	S	**T**	**T x S**
CD (0.05)	0.007	0.012	0.017

4.5.1.16. Microbial biomass carbon (MBC)

Perusal of data presented in Table 49 revealed that, during the main crop the effect of different treatments, except control on MBC was only comparable. Control plots registered significantly lowest MBC (72.91 mg kg^{-1}). As regards the succeeding crop, the highest MBC was recorded in the treatments soil test based POP (169.9 mg kg^{-1}) and biochar 5 t ha^{-1} (159.4 mg kg^{-1}) which were on par with each other. As could be expected, significantly the lowest MBC was recorded in the absolute control (121.4 mg kg^{-1}). The interaction of season with treatments was significant. In all treatments the MBC content increased after vegetable cowpea.

MBC was found to have positive relationship with organic carbon, CEC, dehydrogenase activity, $KMnO_4$-N, NH_4OAc-Mg, HCl-Zn during main crop and with organic carbon, $KMnO_4$-N and $CaCl_2$-S in succeeding crop (Table 33 and 34).

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Table 49. Effect of biochar application on MBC content (mg kg^{-1}) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	72.91	121.4	**97.16**
FYM 10 t ha^{-1}	120.6	144.9	**132.8**
Biochar 5 t ha^{-1}	128.7	159.4	**144.1**
Biochar 7.5 t ha^{-1}	130.0	144.6	**137.3**
Biochar 10 t ha^{-1}	115.9	149.0	**132.5**
Soil test based POP + biochar 10 t ha^{-1}	124.2	150.2	**137.2**
Soil test based POP	129.7	169.9	**149.8**
Season (S) mean	**117.4**	**148.5**	
	S	**T**	**T x S**
CD (0.05)	4.3	8.0	11.4

4.5.1.17. Dehydrogenase activity

The dehydrogenase activity of post-harvest soil as influenced by different treatments is presented in Table 50. In the post-harvest soil of main crop, the highest dehydrogenase activity was recorded in the treatment soil test based POP + biochar (75.04 μg TPF g^{-1} soil 24hr^{-1}) and biochar 10 t ha^{-1} (66.23 μg TPF g^{-1} soil 24hr^{-1}), which was on par with each other. The effect of all other treatments were only comparable and the lowest was associated with control (40.06 μg TPF g^{-1} soil 24hr^{-1}).

In post-harvest soil of second test crop, highest dehydrogenase activity was observed in soil test based POP + biochar (163.6 μg TPF g^{-1} soil 24hr^{-1}), followed by soil test based POP application (116.1 μg TPF g^{-1} soil 24hr^{-1}) and the difference was significant. With an increase in the levels of biochar, dehydrogenase activity increased, however there were no marked differences between them. While comparing the sole application of biochar with NPK + biochar, it was noticed that the dehydrogenase activity got enhanced from 93.12 in the biochar 10 t ha^{-1} to 163.6 μg TPF g^{-1} soil 24hr^{-1} when soil test based NPK application was combined with biochar. Significantly lower values were recorded in control. Further it was noticed that almost in all the treatments, dehydrogenase activity doubled after one more crop was grown.

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Table 50. Effect of biochar application on dehydrogenase activity (µg TPF g^{-1} soil $24hr^{-1}$) in post-harvest soil

Treatments	First season	Second season	Treatment Mean (T)
Control	40.06	61.45	**50.76**
FYM 10 t ha^{-1}	56.07	96.05	**76.06**
Biochar 5 t ha^{-1}	60.31	81.93	**71.12**
Biochar 7.5 t ha^{-1}	61.48	87.93	**74.71**
Biochar 10 t ha^{-1}	66.23	93.12	**79.68**
Soil test based POP + biochar 10 t ha^{-1}	75.04	163.6	**119.3**
Soil test based POP	50.37	116.1	**83.21**
Season (S) mean	**58.51**	**100.0**	
	S	**T**	**T x S**
CD (0.05)	4.79	8.95	12.66

The simple correlation studies among the soil properties had shown that the dehydrogenase activity was significantly and positively correlated with pH, organic carbon, CEC, MBC, $KMnO_4$-N, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B during the main crop (Table 33) and with pH, organic carbon, CEC, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Fe, HCl-Zn and hot water soluble B after the next crop of cowpea (Table 34).

4.5.1.18. Cation exchange capacity (CEC)

The results of the cation exchange capacity of soil after the harvest of two successive crops is shown in Table 51. The initial CEC of the soil was 3.72 cmol (+) kg^{-1} and an increase in the value was observed with the application of biochar. The highest CEC was recorded in the treatments soil test based POP + biochar (4.953 cmol (+) kg^{-1}), biochar 10 t ha^{-1} (4.896 cmol (+) kg^{-1}) and biochar 7.5 t ha^{-1} (4.775 cmol (+) kg^{-1}) which were on par with each other. With an increase in the biochar application rate, CEC increased, although the differences were only marginal. As could be expected, significantly lowest CEC was recorded in absolute control (4.119 cmol (+) kg^{-1}).

The simple correlation studies among the soil properties indicated that the CEC was significantly and positively correlated with pH, organic carbon, MBC, dehydrogenase activity, $KMnO_4$-N, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg and hot water soluble B during the main crop (Table 33) and with pH, organic carbon, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn and HCl-Cu and hot water soluble B in succeeding crop. It was further noticed that the CEC negatively correlated with HCl-Mn (Table 34).

Table 51. Effect of biochar application on CEC and MWHC of post-harvest soil

Treatments	CEC cmol (+) kg^{-1}	MWHC (%)
Control	4.119	30.27
FYM 10 t ha^{-1}	4.443	32.18
Biochar 5 t ha^{-1}	4.553	31.92
Biochar 7.5 t ha^{-1}	4.775	32.82
Biochar 10 t ha^{-1}	4.896	33.31
Soil test based POP + biochar 10 t ha^{-1}	4.953	34.23
Soil test based POP	4.526	32.56
CD (0.05)	**0.264**	**1.25**

4.5.1.19. Maximum water holding capacity (MWHC)

The data furnished in Table 51 shows the positive effect of different treatments on the MWHC of soil. The highest MWHC of 34.23 per cent was recorded in the soils that received soil test based POP + biochar, followed by biochar 10 t ha^{-1} (33.31 %) which were on par with each other. As could be anticipated, with an increase in the biochar levels, MWHC also increased. Significantly lowest MWHC was recorded in absolute control (30.27 %).

4.5.1.20. Fraction of organic matter

4.5.1.20.1. Fulvic acid

Fulvic acid content of soil as influenced by different treatments is presented in Table 52. It was seen from the table that the effect of treatments *viz.* biochar 7.5 t ha^{-1}, biochar 5 t ha^{-1}, biochar 10 t ha^{-1}, soil test based POP + biochar and FYM 10 t ha^{-1} on this parameter were comparable. However, a numerically higher value of 6.53 per cent was registered by two treatments *viz.* biochar 7.5 t ha^{-1} and biochar 5 t ha^{-1}. Significantly lowest fulvic acid was observed in soil test based POP (5.77 %).

Table 52. Effect of biochar application on fraction of organic matter (%) in post-harvest soil

Treatments	Fulvic acid	Humic acid
Control	6.10	2.367
FYM 10 t ha^{-1}	6.40	2.767
Biochar 5 t ha^{-1}	6.53	3.600
Biochar 7.5 t ha^{-1}	6.53	4.567
Biochar 10 t ha^{-1}	6.40	4.633
Soil test based POP + biochar 10 t ha^{-1}	6.40	5.133
Soil test based POP	5.77	3.400
CD (0.05)	**0.29**	**0.725**

4.5.1.20.2. Humic acid

Perusal of data presented in Table 52 revealed that the humic acid content was higher in the soils applied with soil test based POP + biochar (5.133 %), biochar 10 t ha^{-1} (4.633 %) and biochar 7.5 t ha^{-1} (4.567 %) which were all comparable. With an increase in the rate of biochar application, humic acid content increased, although the difference between 7.5 and 10 t ha^{-1} biochar was only marginal. Lowest amount of humic acid was registered in control (2.367 %), which was on par with FYM 10 t ha^{-1} (2.767 %).

4.5.2. Direct effect of biochar on Chinese potato

4.5.2.1. Growth components and yield

4.5.2.1.1. Plant height

Statistical analysis of the data on plant height at harvest is presented *in Table* 53. Plant height ranged from 49.88 to 72.66 cm in all the treatments. It was seen from the results that among different treatments tried, soil test based POP application registered higher plant height (72.66 cm) which was comparable with soil test based POP + biochar (68.05 cm), biochar 5 t ha^{-1} (66.78 cm) and FYM 10 t ha^{-1} (65.53 cm). The lowest plant height was registered by control plots (49.88 cm).

The simple correlation studies unveiled the positive and significant relationship of plant height with tuber girth, DMP and tuber yield (Table 54). It was further noticed that the plant height was positively correlated with the soil properties

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viz. organic carbon, MBC, $KMnO_4$-N, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg, $CaCl_2$-S and HCl-Zn (Table 55).

The stepwise regression analysis including soil properties that significantly correlated with plant height showed that the variation in this parameter could be explained to the extent of 54.9 per cent by MBC and with further inclusion of NH_4OAc-Mg, the variability could be explained to 65.6 per cent (Table 56).

4.5.2.1.2. Average tuber girth

The data on average tuber girth as influenced by treatments is presented in Table 53. It ranged from 2.44 to 3.37 cm in all the treatments. The highest value was recorded in soil test based POP application (3.37 cm), followed by soil test based POP + biochar (3.50 cm) and biochar 7.5 t ha^{-1} (3.32 cm) which were all comparable. Control plots produced tubers with lowest girth (2.44 cm).

Through the simple correlation studies, the positive and significant relationship was noticed between the tuber girth and plant height, DMP, tuber yield, carbohydrates and protein (Table 54). Among the soil properties, organic carbon, CEC, MBC, dehydrogenase activity, Bray-P, NH_4OAc-Mg and $CaCl_2$-S had a positive relationship with the tuber girth (Table 55).

The stepwise regression analysis considering soil properties that significantly correlated with tuber girth revealed that 32.7 per cent variability in the girth of tuber could be altered by the NH_4OAc-Mg status of soil (Table 56).

4.5.2.1.3. Dry matter production

Perusal of data in Table 53 showed that there was significant difference between the treatments with respect to DMP. The highest DMP was observed in soil test based POP application (2959.3 kg ha^{-1}), followed by soil test based POP + biochar (2829.0 kg ha^{-1}) and the difference was significant. The effect of different levels of biochar was only marginal among them. As could be expected, significantly lowest DMP was in the control plots (1767.9 kg ha^{-1}).

Table 53. Effect of biochar application on growth and yield of Chinese potato

Treatments	Plant height (cm)	Average tuber girth (cm)	DMP (kg ha^{-1})	Per plant yield (g)	Tuber yield (t ha^{-1})
Control	49.88	2.44	1767.9	58.79	16.62
FYM 10 t ha^{-1}	65.53	2.84	2486.1	95.23	20.51
Biochar 5 t ha^{-1}	66.78	2.76	2637.2	92.47	20.78
Biochar 7.5 t ha^{-1}	61.86	3.32	2680.8	98.35	20.26
Biochar 10 t ha^{-1}	58.75	3.00	2663.3	101.98	21.34
Soil test based POP + biochar 10 t ha^{-1}	68.05	3.50	2829.0	147.98	24.04
Soil test based POP	72.66	3.37	2959.3	139.53	22.31
CD (0.05)	**8.25**	**0.32**	**105.8**	**18.75**	**1.96**

Table 54. Correlation analysis among the growth, yield and quality attributes of Chinese potato (n = 21)

Parameters	Plant height	Tuber girth	DMP	Tuber yield	CHO	Protein	Crude fibre
Plant height	1.000						
Tuber girth	0.535*	1.000					
DMP	0.765**	0.748**	1.000				
Tuber yield	0.701**	0.720**	0.840**	1.000			
CHO	0.409^{NS}	0.540*	0.744**	0.690**	1.000		
Protein	0.643**	0.731**	0.664**	0.630**	0.339^{NS}	1.000	
Crude fibre	-0.120^{NS}	0.076^{NS}	0.092^{NS}	-0.165^{NS}	0.165^{NS}	-0.100^{NS}	1.000

(** - Significant at 0.01 level, * - Significant at 0.05 level)

Table 55. Correlation analysis between the growth, yield and quality attributes of Chinese potato and the post-harvest soil properties (n = 21)

Parameters		Plant height	Tuber girth	DMP	Tuber yield	CHO	Protein	Crude fibre
pH		0.055^{NS}	0.332^{NS}	0.437*	0.457*	0.774**	-0.004^{NS}	0.176^{NS}
EC		0.428^{NS}	0.426^{NS}	0.372^{NS}	0.546*	0.300^{NS}	0.729**	-0.381^{NS}
Organic C		0.437*	0.533*	0.702**	0.660**	0.815**	0.226^{NS}	0.300^{NS}
CEC		0.348^{NS}	0.556**	0.679**	0.662**	0.838**	0.337^{NS}	0.021^{NS}
MBC		0.741**	0.562**	0.899**	0.701**	0.576**	0.498*	0.129^{NS}
DHY		0.354^{NS}	0.484*	0.642**	0.669**	0.808**	0.255^{NS}	0.053^{NS}
Available nutrient status	**N**	0.463*	0.379^{NS}	0.479*	0.575**	0.467*	0.242^{NS}	-0.084^{NS}
	P	0.588**	0.558**	0.604**	0.640**	0.332^{NS}	0.762**	-0.448*
	K	0.099^{NS}	0.391^{NS}	0.495*	0.464*	0.829**	0.024^{NS}	0.362^{NS}
	Ca	0.435*	0.394^{NS}	0.478*	0.595**	0.551**	0.459*	-0.596**
	Mg	0.659**	0.572**	0.573**	0.680**	0.333^{NS}	0.676**	-0.538*
	S	0.445*	0.539*	0.407^{NS}	0.365^{NS}	0.051^{NS}	0.809**	-0.159^{NS}
	Fe	0.059^{NS}	0.170^{NS}	0.169^{NS}	0.394^{NS}	0.254^{NS}	0.226^{NS}	-0.233^{NS}
	Mn	0.258^{NS}	0.096^{NS}	0.373^{NS}	0.312^{NS}	0.372^{NS}	0.197^{NS}	-0.263^{NS}
	Zn	0.472*	0.370^{NS}	0.425^{NS}	0.541*	0.308^{NS}	0.411^{NS}	-0.303^{NS}
	Cu	-0.015^{NS}	0.031^{NS}	0.287^{NS}	0.261^{NS}	0.428^{NS}	-0.390^{NS}	0.258^{NS}
	B	-0.141^{NS}	0.143^{NS}	0.263^{NS}	0.208^{NS}	0.465*	-0.291^{NS}	0.132^{NS}

(** - Significant at 0.01 level, * - Significant at 0.05 level)

MBC – Microbial biomass carbon, DHY – Dehydrogenase activity

Table 56. Stepwise regression analysis between the growth and quality attributes of Chinese potato and post-harvest soil properties

Y	R^2	Regression equation
Plant height	0.549^{**}	Y = 28.016 + 0.301(MBC)
	0.656^{**}	Y = 14.922 + 0.222(MBC) + 0.358(Mg)
Tuber girth	0.327^{**}	Y = 1.282 + 0.028(Mg)
DMP	0.807^{**}	Y = 613.707 + 16.699(MBC)
	0.871^{**}	Y = 615.674 + 14.552(MBC) + 5.131(P)
	0.907^{**}	Y = 457.905 + 12.696(MBC) + 5.791(P) + 0.669(K)
	0.938^{**}	Y = 4603.45 + 12.49(MBC) + 6.349(P) + 2.442(K) – 918.89(pH)
CHO	0.669^{**}	Y = -10.909 + 5.054(CEC)
Protein	0.649^{**}	Y = 0.796 + 0.080(S)
	0.761^{**}	Y = 0.541 + 0.062(S) + 0.007(Mg)
Crude fibre	0.355^{**}	Y = 18.117 – 0.030(Ca)

The simple correlation studies disclosed the positive and significant relationship of DMP with plant height, tuber girth, tuber yield, carbohydrates, protein and soil properties *viz*. pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-Ca and NH_4OAc-Mg (Table 54 and 55).

The stepwise regression analysis accounting all soil properties that correlated with DMP had shown that MBC alone contributed to the increase in DMP, to the extent of 80.7 per cent and with further inclusion of Bray-P, NH_4OAc-K and pH, variability could be explained to 93.8 per cent (Table 56).

4.5.2.1.4. Per plant yield

In case of per plant yield, there was significant difference between the treatments (Table 53). The highest value was registered in the treatment soil test based POP + biochar (147.98 g), followed by soil test based POP (139.53 g) which were on par with each other but significantly higher than the others. Lowest value was in control plots (58.79 g). The effect of rest of the treatments on tuber yield per plant was only marginal.

4.5.2.1.5. Tuber yield

The tuber yield of Chinese potato plants ranged from 16.62 to 24.04 t ha^{-1} in different treatments (Table 53). The highest tuber yield was recorded in the plots which received soil test based POP + biochar application (24.04 t ha^{-1}), followed by soil test based POP (22.31 t ha^{-1}) which were on par with each other. All other treatments, except control recorded comparable yield. As could be expected, significantly lowest tuber yield was recorded in control plots (16.62 t ha^{-1}).

The simple correlation studies had shown that the tuber yield was positively correlated with plant height, tuber girth and DMP (Table 54). Significant and positive correlation could also be observed between the tuber yield and soil properties *viz.* pH, electrical conductivity, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg and HCl-Zn (Table 55).

4.5.2.1.6. Path analysis

Path coefficients of growth components indicating the direct and indirect effect on tuber yield is given in Table 57. The direct effect of DMP on tuber yield was very high (0.551) and positive, whereas indirect effect of DMP through plant height and tuber girth was moderate and positive (0.122 and 0.166). The direct effect of plant height and tuber girth on tuber yield was moderate and positive (0.160 and 0.222), while the indirect effect though DMP was very high (0.422 and 0.412).

The direct and indirect effect of nutrient content (tuber) on tuber yield as indicated by path coefficients are given in Table 58. Direct effect of Ca and Cu was high (0.317) and very high (0.800), respectively. Direct effect of N and K was moderate and positive, whereas the effect of Fe was negative and moderate (-0.244). All other direct effects were negligible.

Table 59, indicating the direct and indirect effect of nutrient content of haulm on the tuber yield revealed the very high and positive effect of K (0.435) on tuber yield. The indirect effect of N, Fe, Mn and B through K was moderate, whereas the indirect effect of K, Fe and Mn through B was high.

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Table 57. Path coefficients of growth components to the tuber yield

	Plant height	Tuber girth	DMP	Correlation coefficient
Plant height	**0.160**	0.119	0.422	0.701
Tuber girth	0.086	**0.222**	0.412	0.720
DMP	0.122	0.166	**0.551**	0.840

Table 58. Path coefficients of nutrient content of tuber to the tuber yield

	N	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B	Correlation coefficient
N	**0.163**	0.108	0.151	0.046	0.001	-0.110	0.099	-0.456	0.617	0.017	0.636
K	0.095	**0.184**	0.081	0.027	0.000	-0.073	0.129	-0.324	0.368	0.012	0.500
Ca	0.078	0.047	**0.317**	0.049	0.001	-0.097	0.167	-0.344	0.470	0.013	0.699
Mg	0.098	0.063	0.200	**0.077**	0.000	-0.121	0.133	-0.369	0.589	0.017	0.687
S	0.102	0.067	0.172	0.030	**0.001**	-0.103	0.098	-0.326	0.531	0.012	0.582
Fe	0.080	0.061	0.138	0.042	0.000	**-0.224**	0.215	-0.326	0.478	0.016	0.481
Mn	0.043	0.064	0.141	0.027	0.000	-0.128	**0.375**	-0.328	0.418	0.014	0.627
Zn	0.126	0.101	0.185	0.048	0.001	-0.124	0.209	**-0.589**	0.707	0.020	0.685
Cu	0.126	0.085	0.186	0.057	0.001	-0.134	0.196	-0.520	**0.800**	0.021	0.818
B	0.106	0.089	0.155	0.049	0.000	-0.139	0.210	-0.459	0.639	**0.026**	0.676

Table 59. Path coefficients of nutrient content of haulm to the tuber yield

	N	K	Fe	Mn	B	Correlation coefficient
N	**0.053**	0.276	-0.032	0.033	0.179	0.509
K	0.034	**0.435**	-0.115	0.121	0.320	0.794
Fe	0.007	0.216	**-0.232**	0.143	0.406	0.541
Mn	0.009	0.264	-0.166	**0.199**	0.352	0.657
B	-0.020	-0.286	0.194	-0.144	**-0.487**	-0.743

Table 60. Path coefficients of post-harvest soil properties and available nutrient status to the tuber yield

	pH	EC	OC	CEC	MBC	DHY	N	P	K	Ca	Mg	Zn	Correlation coefficient
pH	**-0.325**	0.007	0.540	-0.063	0.054	-0.225	0.011	0.025	0.354	0.075	0.011	-0.007	0.457
EC	-0.015	**0.144**	0.071	-0.021	0.028	-0.103	0.017	0.294	0.002	0.095	0.046	-0.012	0.546
OC	-0.271	0.016	**0.647**	-0.059	0.101	-0.230	0.018	0.047	0.312	0.067	0.021	-0.009	0.660
CEC	-0.282	0.043	0.531	**-0.072**	0.080	-0.230	0.016	0.128	0.309	0.120	0.028	-0.009	0.662
MBC	-0.126	0.028	0.466	-0.041	**0.140**	-0.162	0.018	0.147	0.149	0.060	0.032	-0.010	0.701
DHY	-0.278	0.056	0.564	-0.063	0.086	**-0.263**	0.022	0.132	0.297	0.096	0.031	-0.012	0.669
N	-0.096	0.070	0.332	-0.034	0.071	-0.160	**0.036**	0.151	0.103	0.076	0.038	-0.012	0.575
P	-0.023	0.120	0.086	-0.026	0.058	-0.099	0.015	**0.352**	0.011	0.109	0.050	-0.014	0.640
K	-0.310	0.001	0.544	-0.060	0.056	-0.210	0.010	0.010	**0.371**	0.052	0.004	-0.004	0.464
Ca	-0.139	0.078	0.247	-0.049	0.048	-0.144	0.015	0.218	0.109	**0.176**	0.048	-0.012	0.595
Mg	-0.059	0.105	0.217	-0.033	0.071	-0.131	0.021	0.280	0.024	0.134	**0.063**	-0.015	0.680
Zn	-0.101	0.076	0.255	-0.028	0.062	-0.141	0.019	0.215	0.070	0.094	0.042	**-0.022**	0.541

MBC – Microbial biomass carbon, DHY – Dehydrogenase activity

Path coefficients explaining the direct as well as the indirect effects of different soil properties on tuber yield are presented in Table 60. The direct effect of organic carbon, Bray-P, NH_4OAc-K on tuber yield was very high and positive. With regard to the electrical conductivity, MBC, NH_4OAc-Ca, the direct effect was moderate and positive. The direct effect of pH on tuber yield was high but negative (-0.325). All other direct effects were negligible.

4.5.2.2. Quality attributes of tuber

4.5.2.2.1. Carbohydrates

Data on the effect of treatments on carbohydrate content of tuber is presented in Table 61. The CHO was found to be highest in the treatment biochar 10 t ha^{-1} which was on par with soil test based POP + biochar application but superior to all the other treatments. Significantly lower value was registered by tubers grown in control plots.

The simple correlation studies revealed the positive and significant relationship of CHO with the content of P, Ca, Mg, S, Fe, Mn, Zn, Cu and B in tubers (Table 62).

Table 61. Effect of biochar application on quality attributes of Chinese potato tuber

Treatments	**CHO**	**Protein**	**Crude fibre**
	%		
Control	9.43	1.356	7.00
FYM 10 t ha^{-1}	10.66	1.454	5.83
Biochar 5 t ha^{-1}	12.98	1.380	8.00
Biochar 7.5 t ha^{-1}	12.20	1.537	8.00
Biochar 10 t ha^{-1}	14.48	1.393	7.17
Soil test based POP + biochar 10 t ha^{-1}	14.37	1.682	6.67
Soil test based POP	12.58	1.742	6.83
CD (0.05)	**0.97**	**0.080**	**1.17**

Stepwise regression analysis considering soil properties that correlated with CHO had shown that the variation in this parameter could be significantly explained by CEC of soil ($R^2 = 0.699^{**}$) (Table 56). Furthermore, the stepwise regression analysis between the nutrient content of tuber and CHO revealed that the variation in CHO could be significantly altered by the P and Mn content of tuber, to the extent of 74.9 per cent (Table 63).

4.5.2.2.2. Protein

The highest protein content was observed in soil test based POP application (1.742 %), followed by soil test based POP + biochar (1.682 %) which were on par with each other (Table 61). Lowest protein content was observed in the control plots (1.356 %). However, the treatments biochar 5 t ha^{-1} and biochar 10 t ha^{-1} were on par with control.

Significant and positive relationship was observed between the protein content of tuber and plant height, tuber girth and DMP (Table 54). With respect to the concentration of nutrients in tuber, protein had a positive relationship with all the elements analysed, except Mn (Table 62).

Table 62. Correlation analysis between the nutrient content of tuber and quality attributes of Chinese potato (n = 21)

Parameters		CHO	Protein	Crude fibre
Nutrient content of tuber	N	0.343^{NS}	1.000^{**}	-0.112^{NS}
	P	0.624^{**}	0.498^{*}	0.022^{NS}
	K	0.420^{NS}	0.584^{**}	-0.000^{NS}
	Ca	0.478^{*}	0.474^{*}	-0.023^{NS}
	Mg	0.540^{*}	0.590^{**}	-0.236^{NS}
	S	0.439^{*}	0.624^{**}	0.206^{NS}
	Fe	0.634^{**}	0.486^{*}	0.415^{NS}
	Mn	0.762^{**}	0.256^{NS}	0.109^{NS}
	Zn	0.674^{**}	0.774^{**}	0.054^{NS}
	Cu	0.664^{**}	0.764^{**}	-0.090^{NS}
	B	0.686^{**}	0.640^{**}	-0.145^{NS}

The stepwise regression accounting all soil properties that correlated with protein had shown that 64.9 per cent variability in this parameter could be significantly explained by $CaCl_2$-S status of soil and with further inclusion of NH_4OAc-Mg, 76.1 per cent variability could be explained (Table 56). In addition, the stepwise regression analysis between the nutrient content of tuber and protein revealed that the variation in CHO content of tuber could be attributed to the N contained in tuber ($R^2 = 1.000^{**}$) (Table 63).

Table 63. Stepwise regression analysis between the quality attributes and nutrient content of tuber

Y	R^2	Regression equation
CHO	0.581^{**}	Y = -0.745 + 0.201(Mn)
	0.749^{**}	Y = -17.898 + 0.158(Mn) + 40.296(P)
Protein	1.000^{**}	Y = 0.000 + 1.292(N)

4.4.2.2.3. Crude fibre

Table 61 showed that the crude fibre content was higher in the tubers harvested from plots which received biochar 5 t ha^{-1} and 7.5 t ha^{-1} (8.00 %). However, the treatment biochar 10 t ha^{-1} and control was also on par with those treatments. Lowest crude fibre content was registered by FYM 10 t ha^{-1} (5.83 %).

The stepwise regression analysis including all soil properties that correlated with crude fibre had shown that the variation in this parameter could be significantly explained to 35.5 per cent by NH_4OAc-Ca status of soil (Table 56).

4.5.2.3. Nutrient content and uptake

4.5.2.3.1. Nitrogen content

The data on N content of haulm and tuber is given in Table 64. The highest content of N in haulm was noticed in biochar 10 t ha^{-1} (1.280 %) and lowest in control (0.993 %). Although application of biochar 10 t ha^{-1} recorded highest N in haulm, it was on par with soil test based POP + biochar, biochar 7.5 t ha^{-1}, biochar 5 t ha^{-1} and FYM 10 t ha^{-1}. With respect to the concentration of N in tuber, the treatment soil test based POP and soil test based POP + biochar recorded the highest. Although there was no difference between them, it was significant from rest of the treatments. Lowest value was associated with control plots (1.050 %).

Nitrogen content in the tuber had a significant positive correlation with electrical conductivity, MBC, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg and $CaCl_2$-S (Table 65).

The stepwise regression analysis accounting all soil properties that correlated with the N content in tuber revealed that 76.1 per cent variation in this parameter could be explained with successive addition of the independent variables *viz.* $CaCl_2$-S and NH_4OAc-Mg status of soil (Table 66).

Table 64. Effect of biochar application on nitrogen content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	0.993	1.050	17.56	37.52	55.08
FYM 10 t ha^{-1}	1.193	1.125	29.65	48.20	77.85
Biochar 5 t ha^{-1}	1.203	1.068	31.71	46.20	77.91
Biochar 7.5 t ha^{-1}	1.245	1.190	33.38	50.31	83.70
Biochar 10 t ha^{-1}	1.280	1.078	34.08	47.77	81.84
Soil test based POP + biochar 10 t ha^{-1}	1.277	1.302	36.13	60.38	96.51
Soil test based POP	1.068	1.348	31.58	59.70	91.28
CD (0.05)	**0.099**	**0.062**	**2.31**	**3.00**	**3.82**

4.5.2.3.2. Nitrogen uptake

Perusal of data revealed that there was significant difference between the treatments with respect to the uptake of N (Table 64). N uptake by haulm was found to be higher in the treatments soil test based POP + biochar (36.13 kg ha^{-1}) and biochar 10 t ha^{-1} (34.08 kg ha^{-1}). In case of N uptake by tuber, again the treatment soil test based POP + biochar recorded the highest value, however it was on par with soil test based POP. Regarding the total N uptake, the treatment soil test based POP + biochar recorded significantly higher value (96.51 kg ha^{-1}), and it was followed by soil test based POP (91.28 kg ha^{-1}). The difference was significant as well. Uptake of N by haulm, tuber and total was found to be significantly low in the control plots.

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Table 65. Correlation analysis between the nutrient content of tuber and the post-harvest soil properties (n = 21)

Parameters		Nutrient content of tuber										
		N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH		-0.005^{NS}	0.409^{NS}	0.411^{NS}	0.380^{NS}	0.229^{NS}	0.169^{NS}	0.430^{NS}	0.640^{**}	0.307^{NS}	0.229^{NS}	0.451^{*}
EC		0.735^{**}	0.304^{NS}	0.377^{NS}	0.216^{NS}	0.571^{**}	0.319^{NS}	0.273^{NS}	0.213^{NS}	0.433^{*}	0.518^{*}	0.522^{*}
OC		0.226^{NS}	0.340^{NS}	0.416^{NS}	0.508^{*}	0.300^{NS}	0.461^{*}	0.608^{**}	0.727^{**}	0.440^{*}	0.449^{*}	0.417^{NS}
CEC		0.337^{NS}	0.574^{**}	0.556^{**}	0.618^{**}	0.512^{*}	0.440^{*}	0.509^{*}	0.591^{**}	0.526^{*}	0.497^{*}	0.558^{**}
MBC		0.499^{*}	0.324^{NS}	0.480^{*}	0.616^{**}	0.493^{*}	0.673^{**}	0.471^{*}	0.585^{**}	0.602^{**}	0.682^{**}	0.371^{NS}
DHY		0.258^{NS}	0.409^{NS}	0.488^{*}	0.457^{*}	0.467^{*}	0.352^{NS}	0.510^{*}	0.652^{**}	0.373^{NS}	0.431^{NS}	0.484^{*}
Available nutrient status	N	0.244^{NS}	0.184^{NS}	0.185^{NS}	0.345^{NS}	0.358^{NS}	0.412^{NS}	0.263^{NS}	0.409^{NS}	0.227^{NS}	0.381^{NS}	0.222^{NS}
	P	0.767^{**}	0.511^{*}	0.467^{*}	0.380^{NS}	0.613^{**}	0.478^{*}	0.209^{NS}	0.315^{NS}	0.600^{**}	0.704^{**}	0.586^{**}
	K	0.023^{NS}	0.423^{NS}	0.378^{NS}	0.424^{NS}	0.226^{NS}	0.250^{NS}	0.537^{*}	0.681^{**}	0.401^{NS}	0.305^{NS}	0.467^{*}
	Ca	0.466^{*}	0.602^{**}	0.483^{*}	0.397^{NS}	0.531^{*}	0.279^{NS}	0.121^{NS}	0.362^{NS}	0.479^{*}	0.495^{*}	0.563^{**}
	Mg	0.682^{**}	0.446^{*}	0.471^{*}	0.403^{NS}	0.528^{*}	0.470^{*}	0.211^{NS}	0.250^{NS}	0.486^{*}	0.626^{**}	0.556^{**}
	S	0.803^{**}	0.334^{NS}	0.556^{**}	0.206^{NS}	0.403^{NS}	0.429^{NS}	0.125^{NS}	-0.048^{NS}	0.492^{*}	0.504^{*}	0.340^{NS}
	Fe	0.227^{NS}	0.315^{NS}	0.189^{NS}	0.194^{NS}	0.210^{NS}	0.305^{NS}	-0.014^{NS}	0.057^{NS}	0.203^{NS}	0.207^{NS}	0.422^{NS}
	Mn	0.202^{NS}	0.511^{*}	0.429^{NS}	-0.122^{NS}	0.112^{NS}	0.255^{NS}	0.022^{NS}	0.260^{NS}	0.388^{NS}	0.417^{NS}	0.426^{NS}
	Zn	0.415^{NS}	0.264^{NS}	0.589^{**}	0.216^{NS}	0.328^{NS}	0.181^{NS}	0.180^{NS}	0.482^{*}	0.295^{NS}	0.372^{NS}	0.354^{NS}
	Cu	-0.385^{NS}	0.124^{NS}	0.106^{NS}	0.158^{NS}	-0.082^{NS}	0.186^{NS}	0.058^{NS}	0.341^{NS}	-0.024^{NS}	0.060^{NS}	0.078^{NS}
	B	-0.291^{NS}	0.114^{NS}	0.170^{NS}	0.304^{NS}	-0.134^{NS}	0.070^{NS}	0.119^{NS}	0.560^{**}	0.090^{NS}	0.003^{NS}	0.172^{NS}

Table 66. Stepwise regression analysis between the nutrient content of tuber and post-harvest soil properties

Y	R^2	Regression equation
N	0.650^{**}	Y = 0.616 + 0.062(S)
	0.761^{**}	Y = 0.419 + 0.048(S) + 0.005(Mg)
P	0.364^{**}	Y = 0.311 + 0.040(CEC)
K	0.343^{**}	Y = 2.240 +0.068(Zn)
Ca	0.394^{**}	Y = -0.096 + 0.109(CEC)
Mg	0.384^{**}	Y = 0.140 + 0.001(P)
S	0.474^{**}	Y = 0.064 + 0.0001(MBC)
Fe	0.348^{**}	Y = 115.801 + 423.339(OC)
Mn	0.516^{**}	Y = -29.939 + 54.565(OC)
Zn	0.362^{**}	Y = 18.071 + 0.154(MBC)
	0.509^{**}	Y = 18.113 + 0.109(MBC) + 0.108 (P)
Cu	0.496^{**}	Y = 22.734 + 0.079(P)
	0.678^{**}	Y = 17.620 + 0.057(P) + 0.053(MBC)
B	0.343^{**}	Y = 23.01 + 0.097(P)
	0.546^{**}	Y = 16.606 + 0.094(P) + 0.013(K)

Total N uptake had a significant positive correlation with pH, electrical conductivity, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, $CaCl_2$-S and HCl-Zn (Table 67).

Around 93.1 per cent variation in the total N uptake could be significantly explained through stepwise regression analysis with successive addition of the independent variables *viz*. MBC, electrical conductivity and CEC of soil (Table 68).

4.5.2.3.3. Phosphorus content

Phosphorus content in haulm and tuber of plants that received different treatments varied significantly (Table 69). Concentration of P in haulm was found to be maximum in the plots which received biochar 10 t ha^{-1} (0.563 %). However, it was on par with the treatments biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1}. The lowest was in control plots (0.369 %).

Of the different treatments tried, higher concentration of P in tuber was observed for biochar 10 t ha^{-1} and soil test based POP which were on par with each other. The treatment, control recorded lowest P content in tuber (0.473 %). However, it was on par with FYM 10 t ha^{-1} and biochar 5 t ha^{-1}.

Table 67. Correlation analysis between the nutrient uptake by Chinese potato and the post-harvest soil properties (n = 21)

Parameters		Total nutrient uptake										
		N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH		0.497^{*}	0.666^{**}	0.509^{*}	0.662^{**}	0.619^{**}	0.672^{**}	0.482^{*}	0.334^{NS}	0.623^{**}	0.489^{*}	0.371^{NS}
EC		0.582^{**}	0.125^{NS}	0.537^{*}	0.088^{NS}	0.340^{NS}	0.108^{NS}	0.415^{NS}	0.621^{**}	0.216^{NS}	0.387^{NS}	0.182^{NS}
OC		0.711^{**}	0.802^{**}	0.755^{**}	0.749^{**}	0.712^{**}	0.825^{**}	0.724^{**}	0.527^{*}	0.745^{**}	0.709^{**}	0.540^{*}
CEC		0.752^{**}	0.745^{**}	0.752^{**}	0.778^{**}	0.780^{**}	0.767^{**}	0.702^{**}	0.602^{**}	0.722^{**}	0.699^{**}	0.425^{NS}
MBC		0.827^{**}	0.811^{**}	0.849^{**}	0.780^{**}	0.820^{**}	0.869^{**}	0.825^{**}	0.697^{**}	0.770^{**}	0.830^{**}	0.730^{**}
DHY		0.724^{**}	0.723^{**}	0.771^{**}	0.666^{**}	0.750^{**}	0.725^{**}	0.663^{**}	0.570^{**}	0.684^{**}	0.653^{**}	0.601^{**}
Available nutrient status	N	0.557^{**}	0.441^{*}	0.619^{**}	0.403^{NS}	0.427^{NS}	0.386^{NS}	0.485^{*}	0.470^{*}	0.408^{NS}	0.518^{*}	0.638^{**}
	P	0.708^{**}	0.364^{NS}	0.657^{**}	0.377^{NS}	0.610^{**}	0.387^{NS}	0.565^{**}	0.752^{**}	0.468^{*}	0.594^{**}	0.424^{NS}
	K	0.506^{*}	0.704^{**}	0.528^{*}	0.720^{**}	0.625^{**}	0.679^{**}	0.557^{**}	0.366^{NS}	0.684^{**}	0.563^{**}	0.335^{NS}
	Ca	0.630^{**}	0.411^{NS}	0.590^{**}	0.411^{NS}	0.537^{*}	0.438^{*}	0.464^{*}	0.643^{**}	0.487^{*}	0.517^{*}	0.383^{NS}
	Mg	0.726^{**}	0.352^{NS}	0.686^{**}	0.343^{NS}	0.531^{*}	0.457^{*}	0.532^{*}	0.710^{**}	0.432^{NS}	0.569^{**}	0.523^{*}
	S	0.498^{*}	0.082^{NS}	0.450^{*}	0.097^{NS}	0.343^{NS}	0.161^{NS}	0.347^{NS}	0.467^{*}	0.216^{NS}	0.318^{NS}	-0.009^{NS}
	Fe	0.292^{NS}	0.228^{NS}	0.210^{NS}	0.152^{NS}	0.194^{NS}	0.252^{NS}	0.180^{NS}	0.240^{NS}	0.202^{NS}	0.212^{NS}	0.121^{NS}
	Mn	0.335^{NS}	0.461^{*}	0.364^{NS}	0.321^{NS}	0.369^{NS}	0.447^{*}	0.320^{NS}	0.442^{*}	0.445^{*}	0.397^{NS}	0.312^{NS}
	Zn	0.580^{**}	0.323^{NS}	0.593^{**}	0.328^{NS}	0.517^{*}	0.387^{NS}	0.405^{NS}	0.510^{*}	0.372^{NS}	0.403^{NS}	0.447^{*}
	Cu	0.160^{NS}	0.573^{**}	0.254^{NS}	0.514^{*}	0.347^{NS}	0.551^{**}	0.240^{NS}	0.070^{NS}	0.433^{NS}	0.326^{NS}	0.614^{**}
	B	0.201^{NS}	0.578^{**}	0.181^{NS}	0.563^{**}	0.380^{NS}	0.628^{**}	0.233^{NS}	0.057^{NS}	0.454^{*}	0.278^{NS}	0.395^{NS}

MBC – Microbial biomass carbon, DHY – Dehydrogenase activity

Table 68. Stepwise regression analysis between the total nutrient uptake (Chinese potato) and post-harvest soil properties

Y	R^2	Regression equation
N	0.684^{**}	Y = 18.882 + 0.526(MBC)
	0.878^{**}	Y = -1.560 + 0.482(MBC) + 433.155(EC)
	0.931^{**}	Y = - 42.924 + 0.382(MBC) + 370.693(EC) + 12.33(CEC)
P	0.658^{**}	Y = 10.94 + 0.190(MBC)
	0.828^{**}	Y = 6.702 + 0.148(MBC) + 0.018(K)
	0.868^{**}	Y = -0.515 + 0.136(MBC) + 0.017(K) + 0.231(Mn)
K	0.720^{**}	Y = 25.939 + 1.912(MBC)
	0.863^{**}	Y = -36.205 + 1.781(MBC) + 1316.83(EC)
	0.917^{**}	Y = -184.045 + 1.422(MBC) + 1093.582(EC) + 44.068(CEC)
Ca	0.608^{**}	Y = 11.565 + 0.449(MBC)
	0.805^{**}	Y = 0.353 + 0.337(MBC) + 0.047(K)
	0.862^{**}	Y = 107.194 + 0.514(MBC) + 0.091(K) – 85.953(OC)
Mg	0.673^{**}	Y = 3.027 + 0.107(MBC)
	0.816^{**}	Y = -11.35 + 0.073(MBC) + 4.0(CEC)
	0.871^{**}	Y = -9.847 + 0.062(MBC) + 3.586(CEC) + 0.034(P)
	0.905^{**}	Y = -7.349 + 0.069(MBC) + 3.898(CEC) + 0.064(P) – 0.099(Mg)
S	0.755^{**}	Y = 0.390 + 0.106(MBC)
	0.887^{**}	Y = -19.912 + 0.088(MBC) + 4.087(pH)
Fe	0.681^{**}	Y = 2.234 + 0.048(MBC)
	0.759^{**}	Y = -2.449 + 0.036(MBC) + 1.303(CEC)
Mn	0.569^{**}	Y = 0.725 + 0.011(P)
	0.746^{**}	Y = -1.70 + 0.011(P) + 1.411(OC)
Zn	0.602^{**}	Y = 0.051 + 0.003(MBC)
	0.766^{**}	Y = -0.011 + 0.002(MBC) + 0.0001(K)
	0.816^{**}	Y = -0.017 + 0.002(MBC) + 0.0001(K) + 0.001(P)
Cu	0.720^{**}	Y = 0.046 + 0.001(MBC)
	0.786^{**}	Y = -0.062 + 0.001(MBC) + 0.030(CEC)
B	0.514^{**}	Y = 0.190 + 0.001(MBC)
	0.680^{**}	Y = 0.084 + 0.001(MBC) + 0.067(Cu)
	0.777^{**}	Y = 0.020 + 0.0001(MBC) + 0.083(Cu) + 0.001(Mg)

The simple correlation studies indicated the positive and significant relationship of P content (tuber) with CEC, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg and HCl-Mn (Table 65).

Furthermore, the stepwise regression analysis considering all soil properties that correlated with P content (tuber) revealed that the variation in the concentration of P in tuber could be attributed to the CEC of soil ($R^2 = 0.364^{**}$) (Table 66).

Table 69. Effect of biochar application on phosphorus content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	0.369	0.473	6.53	16.90	23.43
FYM 10 t ha^{-1}	0.436	0.484	10.87	20.71	31.58
Biochar 5 t ha^{-1}	0.533	0.479	14.02	20.71	34.74
Biochar 7.5 t ha^{-1}	0.515	0.493	13.80	20.83	34.62
Biochar 10 t ha^{-1}	0.563	0.52	15.00	23.05	38.05
Soil test based POP + biochar 10 t ha^{-1}	0.422	0.504	11.95	23.36	35.30
Soil test based POP	0.412	0.515	12.21	22.80	35.01
CD (0.05)	**0.109**	**0.022**	**2.98**	**0.89**	**2.80**

4.5.2.3.4. Phosphorus uptake

Statistical analysis of data presented in Table 69 indicated that there was significant difference between the treatments. The uptake of P by haulm was found to be the highest in biochar 10 t ha^{-1} (15.0 kg ha^{-1}). However, it was on par with the application of biochar 5 t ha^{-1}, biochar 7.5 t ha^{-1} and soil test based POP. The lowest value of 6.53 kg ha^{-1} was recorded in the control.

With respect to the P uptake by tuber, the effect was shared by three treatments *viz.* soil test based POP + biochar, biochar 10 t ha^{-1} and soil test based POP. However, these treatments differed significantly from others. Significantly lowest uptake was in control plots (16.90 kg ha^{-1}).

Considering the total P uptake, it was highest in the treatment biochar 10 t ha^{-1}, followed by soil test based POP + biochar application which were comparable. Significantly lowest uptake was associated with the control plots (23.43 kg ha^{-1}).

The simple correlation studies had shown that the total P uptake was positively correlated with pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, NH_4OAc-K, HCl-Mn, HCl-Cu and hot water soluble B (Table 67).

Stepwise regression analysis had shown that the variation in total P uptake could be significantly explained to the extent of 86.8 per cent with successive addition of independent variables *viz.* MBC, NH_4OAc-K and HCl-Mn status of soil (Table 68).

4.5.2.3.5. Potassium content

Data pertaining to the effect of various treatments on the content of K in haulm and tuber is presented in Table 70. The content of K in haulm was found to be significantly highest in the treatment soil test based POP + biochar (6.31 %) and the lowest was in control (3.785 %). The effect of all other treatments on this parameter was only comparable.

The content of K in tuber did not vary much due to imposed treatments.

The simple correlation analysis disclosed that the K content of tuber was positively correlated with the soil properties *viz.* CEC, MBC, dehydrogenase activity, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg, $CaCl_2$-S and HCl-Zn (Table 65).

Table 70. Effect of biochar application on potassium content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	3.785	2.557	66.93	91.28	158.2
FYM 10 t ha^{-1}	5.174	2.637	128.6	112.9	241.5
Biochar 5 t ha^{-1}	5.508	2.568	145.3	111.1	256.5
Biochar 7.5 t ha^{-1}	5.227	2.718	140.3	114.9	255.2
Biochar 10 t ha^{-1}	5.142	2.68	136.9	118.7	255.7
Soil test based POP + biochar 10 t ha^{-1}	6.31	2.758	178.4	127.9	306.4
Soil test based POP	5.442	2.687	161.3	119.0	280.3
CD (0.05)	**0.622**	**NS**	**20.5**	**6.8**	**22.8**

The step wise regression analysis including soil properties that significantly correlated with the K content of tuber had shown that the variation in K content could be significantly explained by HCl-Zn content of soil ($R^2 = 0.343^{**}$) (Table 66).

4.5.2.3.6. Potassium uptake

Uptake of potassium by plants receiving different treatments varied significantly (Table 70). Potassium uptake by haulm was higher in the treatments soil test based POP + biochar (178.4 kg ha^{-1}) and soil test based POP application (161.3 kg ha^{-1}) which were comparable but superior to rest of the treatments. Application of biochar at different levels had a comparable effect on this parameter.

Significantly higher K uptake by tuber was recorded in the treatment soil test based POP + biochar (127.9 kg ha^{-1}). Superiority of this treatment was evident also in the case of total K uptake, recording a maximum of 306.4 kg ha^{-1}. This was followed by the treatment soil test based POP, which recorded an uptake of 280.3 kg ha^{-1}. Effect of all other treatments on the total K uptake was only marginal. As could be expected, the uptake of K by haulm, tuber and thus the total was found to be lowest in the control plots (66.93, 91.28 and 158.2 kg ha^{-1}, respectively).

The simple correlation studies had shown that the total K uptake was positively correlated with pH, electrical conductivity, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, $CaCl_2$-S and HCl-Zn (Table 67).

The stepwise regression analysis yielded equations that could explain 91.7 per cent variability in total K uptake by plants through MBC, electrical conductivity and cation exchange capacity (Table 68).

4.5.2.3.7. Calcium content

Treatment effect was significant as regards calcium content of haulm and tuber of the plants (Table 71). The treatment biochar 10 t ha^{-1} registered significantly highest content of Ca in haulm (2.152 %). Lowest Ca content of haulm was observed in control (1.631 %). However, it was on par with the treatments soil test based POP (1.690 %) and soil test based POP + biochar application (1.679 %).

Although the content of Ca in tuber was higher in treatment biochar 7.5 t ha^{-1} (0.445 %), it was on par with all other treatments except control, which recorded the lowest Ca content (0.328 %).

The simple correlation studies had shown that the Ca content of tuber was positively correlated with organic carbon, CEC, MBC and dehydrogenase activity (Table 65).

The stepwise regression considering all soil properties that significantly correlated with Ca content of tuber indicated that the variability in this parameter could be significantly attributed to CEC of soil ($R^2 = 0.394^{**}$) (Table 66).

Table 71. Effect of biochar application on calcium content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	1.631	0.328	28.84	11.71	40.55
FYM 10 t ha^{-1}	1.755	0.386	43.64	16.54	60.19
Biochar 5 t ha^{-1}	1.834	0.400	48.33	17.30	65.63
Biochar 7.5 t ha^{-1}	1.935	0.445	51.87	18.80	70.67
Biochar 10 t ha^{-1}	2.152	0.411	57.34	18.21	75.55
Soil test based POP + biochar 10 t ha^{-1}	1.679	0.437	47.49	20.27	67.76
Soil test based POP	1.690	0.444	49.94	19.71	69.65
CD (0.05)	**0.214**	**0.07**	**5.65**	**3.52**	**6.95**

4.5.2.3.8. Calcium uptake

Statistical scrutiny of the data presented in the Table 71 showed that there was significant difference between the treatments tried with respect to the uptake of Ca. In case of haulm, it was found to be higher in biochar 10 t ha^{-1} (57.34 kg ha^{-1}) though on par with the treatment biochar 7.5 t ha^{-1} (51.87 kg ha^{-1}). Significantly lowest Ca uptake by haulm was recorded in the control (28.84 kg ha^{-1}).

Uptake of Ca by tuber was the highest in the plots that received soil test based POP + biochar (20.27 kg ha^{-1}) followed by rest of the treatments which were comparable. Significantly lowest value was recorded in control plots (11.71 kg ha^{-1}).

The total uptake of Ca by plants was higher in the treatments which included biochar 10 t ha^{-1}, biochar 7.5 t ha^{-1} and soil test based POP which were on par with each other. The lowest total Ca uptake was registered in control plots (40.55 kg ha^{-1}).

The simple correlation studies had revealed that the total Ca uptake was positively correlated with pH, organic carbon, CEC, MBC, dehydrogenase activity, NH_4OAc-K, HCl-Cu and hot water soluble B (Table 67).

The stepwise regression analysis yielded equations that could explain 86.2 per cent variability in the total Ca uptake through MBC, NH_4OAc-K and organic carbon (Table 68).

4.5.2.3.9. Magnesium content

The data on concentration of Mg in haulm and tuber of Chinese potato is presented in the Table 72. Highest Mg content of 0.379 per cent in haulm was recorded in biochar 10 t ha^{-1} and it was on par with biochar 7.5 t ha^{-1} and FYM 10 t ha^{-1}. Lowest Mg content in haulm was recorded in the control plots (0.282 %). However, it was on par with soil test based POP + biochar and soil test based POP application. As regards the tuber, the highest Mg content was recorded in the treatments which included soil test based POP, soil test based POP + biochar and biochar 10 t ha^{-1} which were on par with each other. The lowest was in control (0.144 %).

Table 72. Effect of biochar application on magnesium content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	0.282	0.144	4.997	5.137	10.13
FYM 10 t ha^{-1}	0.343	0.158	8.553	6.753	15.31
Biochar 5 t ha^{-1}	0.314	0.162	8.273	7.013	15.29
Biochar 7.5 t ha^{-1}	0.367	0.153	9.847	6.473	16.31
Biochar 10 t ha^{-1}	0.379	0.169	10.10	7.493	17.59
Soil test based POP + biochar 10 t ha^{-1}	0.323	0.18	9.137	8.363	17.50
Soil test based POP	0.315	0.182	9.327	8.087	17.41
CD (0.05)	**0.041**	**0.02**	**1.239**	**0.964**	**1.50**

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The simple correlation studies disclosed that the Mg content of tuber was positively correlated with electrical conductivity, CEC, MBC, dehydrogenase activity, Bray-P, NH_4OAc-Ca and NH_4OAc-Mg (Table 65).

Stepwise regression analysis accounting all soil properties that significantly correlated with Mg content of tuber indicated that the variation in this parameter could be significantly attributed to Bray-P content of soil ($R^2 = 0.384^{**}$) (Table 66).

4.5.2.3.10. Magnesium uptake

The uptake of Mg by haulm was found to be higher in the treatment biochar 10 t ha^{-1} which was comparable with biochar 7.5 t ha^{-1}, soil test based POP and soil test based POP + biochar application. Significantly the lowest Mg uptake was in control plots. Considering the Mg uptake by tuber, it was higher in the treatments which included soil test based POP + biochar, soil test based POP and biochar 10 t ha^{-1} and the lowest was in control plots.

Regarding the total Mg uptake by plants, the treatments biochar 10 t ha^{-1}, soil test based POP + biochar and soil test based POP application recorded higher values. Effect of the treatments FYM 10 t ha^{-1}, biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1} was comparable. Significantly lowest total Mg uptake was registered in control plots.

Total Mg uptake by plants had significant positive correlation with pH, organic carbon, CEC, MBC, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Mg and HCl-Zn (Table 67).

The stepwise regression analysis including all the soil properties that correlated with total Mg uptake revealed that 60.8 per cent variation in this parameter could be explained by the MBC status of soil. Further with successive inclusion of independent variables *viz.* CEC, Bray-P and NH_4OAc-Mg, variability could be explained to 90.5 per cent (Table 68).

4.5.2.3.11. Sulphur content

The concentration of S in haulm and tuber as influenced by different treatments is presented in Table 73. In haulm, the concentration of S was found to be

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higher in the treatments biochar 7.5 t ha^{-1} and biochar 10 t ha^{-1} which were on par with each other, but superior to rest of the treatments.

With respect to concentration of S in tuber, the treatment soil test based POP application registered significantly higher value and it was followed by biochar 7.5 t ha^{-1} and soil test based POP + biochar application. In both haulm and tuber, significantly lower values were associated with the control plots.

Sulphur content (tuber) had significant positive correlation with organic carbon, CEC, MBC, Bray-P and NH_4OAc-Mg (Table 65).

Stepwise regression analysis inclusive of all soil properties that correlated with S content (tuber) further revealed that 47.4 per cent variability in this parameter could be explained by MBC alone (Table 66).

Table 73. Effect of biochar application on sulphur content and uptake of Chinese potato

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	0.237	0.093	4.197	3.330	7.53
FYM 10 t ha^{-1}	0.333	0.106	8.270	4.537	12.81
Biochar 5 t ha^{-1}	0.302	0.111	7.963	4.817	12.78
Biochar 7.5 t ha^{-1}	0.378	0.117	10.13	4.943	15.07
Biochar 10 t ha^{-1}	0.374	0.109	9.950	4.817	14.76
Soil test based POP + biochar 10 t ha^{-1}	0.296	0.117	8.387	5.440	13.82
Soil test based POP	0.27	0.123	8.010	5.447	13.46
CD (0.05)	**0.032**	**0.009**	**0.816**	**0.372**	**0.90**

4.5.2.3.12. Sulphur uptake

The uptake of S by the plants receiving different treatments varied significantly (Table 73). The highest uptake of S by haulm was recorded in the treatments biochar 7.5 t ha^{-1} and biochar 10 t ha^{-1} which were comparable, but superior to rest of the treatments. All other treatments, except control had a comparable effect on this parameter.

As regards the uptake of S by tuber, the higher value was associated with two treatments *viz.* soil test based POP and soil test based POP + biochar application, which differed significantly from all other treatments.

Considering the total S uptake by plants, application of biochar at 7.5 t ha^{-1} and 10 t ha^{-1} showed a significant effect by removing 15.07 and 14.76 kg S from soil per ha, respectively. As could be expected, the uptake of S by haulm, tuber and thus the total was found to be lowest in the control plots.

Total S uptake by plants had significant positive correlation with pH, organic carbon, CEC, MBC, dehydrogenase activity, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Mn, HCl-Cu and hot water soluble boron (Table 67).

The stepwise regression analysis yielded equations that could explain 88.7 per cent variability in the total S uptake through MBC and pH of soil (Table 68).

4.5.2.3.13. Iron content

The concentration of Fe in haulm and tuber varied significantly with treatments (Table 74). Significantly higher concentration of Fe in haulm (1711.0 mg kg^{-1}) was recorded by soil test based POP application. The effect of different treatments *viz.* biochar 5, 7.5 and 10 t ha^{-1} and soil test based POP + biochar on this parameter was only comparable. The treatments control and FYM 10 t ha^{-1} recorded the lowest value of 1538.3 and 1535.8 mg kg^{-1}, respectively which were on par with each other.

The Fe content of tuber in treatments biochar 5, 7.5 and 10 t ha^{-1}, soil test based POP + biochar and soil test based POP were on par with each other, but significantly higher than control. As seen in the case of haulm Fe content, the treatments control and FYM 10 t ha^{-1} registered the lowest value with respect to the Fe content in tuber.

Simple correlation studies further indicated the positive relationship of Fe content (tuber) with organic carbon, CEC, MBC, dehydrogenase activity and NH_4OAc-K of soil (Table 65).

The stepwise regression analysis including all soil properties that correlated with Fe content (tuber) yielded the equation with organic carbon as the dominant independent variable that could explain 34.8 per cent variability in this parameter (Table 66).

Table 74. Effect of biochar application on iron content and uptake of Chinese potato

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	1538.3	791.3	2.720	2.823	5.543
FYM 10 t ha^{-1}	1535.8	756.4	3.819	3.239	7.058
Biochar 5 t ha^{-1}	1623.3	871.8	4.281	3.773	8.054
Biochar 7.5 t ha^{-1}	1594.5	879.3	4.274	3.715	7.989
Biochar 10 t ha^{-1}	1643.0	874.5	4.376	3.877	8.253
Soil test based POP + biochar 10 t ha^{-1}	1631.8	908.2	4.616	4.210	8.826
Soil test based POP	1711.0	904.5	5.062	4.007	9.070
CD (0.05)	**37.5**	**76.2**	**0.184**	**0.273**	**0.342**

4.5.2.3.14. Iron uptake

The uptake of Fe by haulm was found to be the highest in the treatment soil test based POP (5.062 kg ha^{-1}), followed by soil test based POP + biochar application (4.616 kg ha^{-1}) and the difference was significant also. The effect of different levels of biochar on Fe uptake by haulm was only comparable (Table 74). As regards the uptake by tuber, the highest value of 4.210 kg ha^{-1} was noticed in the treatment soil test based POP + biochar application. However, it was on par with soil test based POP (4.007 kg ha^{-1}).

Total Fe uptake by plant was significantly higher in the treatments soil test based POP (9.070 kg ha^{-1}) and soil test based POP + biochar application (8.826 kg ha^{-1}) which were comparable with each other, but superior to rest of the treatments. Significantly lowest Fe uptake by haulm, tuber and in turn the total was registered by control plots.

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The simple correlation studies showed the positive and significant relationship of total Fe uptake with pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca and NH_4OAc-Mg (Table 67).

The stepwise regression analysis accounting all soil properties that correlated with the total Fe uptake had shown that the variation in this parameter could be significantly explained by MBC and CEC of soil ($R^2 = 0.759^{**}$) (Table 68).

4.5.2.3.15. Manganese content

The concentration of Mn in haulm and tuber as affected by different treatments is presented in Table 75. Mn content in haulm was found to be the highest in the treatment soil test based POP (471.3 mg kg^{-1}), followed by soil test based POP + biochar application (454.5 mg kg^{-1}) which were on par with each other but superior to all other treatments. The lowest Mn content was registered in control plots (316.3 mg kg^{-1}), which was comparable with biochar 7.5 t ha^{-1} and biochar 5 t ha^{-1}.

The highest Mn content in tuber was observed in two treatments *viz.* biochar 10 t ha^{-1} and soil test based POP + biochar application, which was on par with biochar 5 t ha^{-1}, biochar 7.5 t ha^{-1} and soil test based POP application. Significantly lowest Mn content was observed in the tubers harvested from control plots (54.33 mg kg^{-1}).

Table 75. Effect of biochar application on manganese content and uptake of Chinese potato

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Haulm	**Tuber**	**Haulm**	**Tuber**	**Total**
Control	316.3	54.33	0.560	0.194	0.754
FYM 10 t ha^{-1}	374.0	62.50	0.929	0.268	1.197
Biochar 5 t ha^{-1}	345.3	66.67	0.911	0.288	1.199
Biochar 7.5 t ha^{-1}	324.8	66.83	0.870	0.282	1.153
Biochar 10 t ha^{-1}	393.2	71.00	1.047	0.315	1.362
Soil test based POP + biochar 10 t ha^{-1}	454.5	70.83	1.285	0.329	1.614
Soil test based POP	471.3	65.33	1.395	0.290	1.684
CD (0.05)	**45.8**	**7.94**	**0.101**	**0.037**	**0.102**

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Through the simple correlation studies, the positive and significant relationship was studied between the Fe content (tuber) and pH, organic carbon, CEC, MBC, dehydrogenase activity, NH_4OAc-K, HCl-Zn and hot water soluble boron (Table 65).

Similar to that of the Fe content, the stepwise regression between the soil properties and Mn content (Tuber) yielded the equation with organic carbon as the dominant independent variable that could explain 51.6 per cent variability in Mn content (Table 66).

4.5.2.3.16. Manganese uptake

Perusal of data presented in Table 75 revealed that there was significant difference between treatments with respect to the uptake of Mn. Significantly higher Mn uptake by haulm was recorded in soil test based POP (1.395 kg ha^{-1}). It was followed by soil test based POP and biochar 10 t ha^{-1}, which differed significantly not only among themselves but also from rest of the treatments.

With regard to the Mn uptake by tuber, the maximum uptake was recorded in the plot that received soil test based POP + biochar (0.329 kg ha^{-1}) and it was on par with biochar 10 t ha^{-1} (0.315 kg ha^{-1}). The effect of all other treatments, except control was only comparable.

The total Mn uptake was found to be maximum in the treatments soil test based POP and soil test based POP + biochar application which were on par with each other but superior to all other treatments. This was followed by application of biochar at 10 t ha^{-1}. As could be expected, significantly lowest Mn uptake by haulm, tuber and their total was recorded by the control treatment.

Among the soil properties, the total Mn uptake had a significant positive relationship with electrical conductivity, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg, $CaCl_2$-S, HCl-Mn and HCl-Zn (Table 67).

Stepwise regression analysis including the soil properties that correlated with total Mn uptake had shown that its variation could be significantly explained by the soil properties *viz*. Bray-P and organic carbon ($R^2 = 0.759^{**}$) (Table 68).

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4.5.2.3.17. Zinc content

The results of statistical analysis had shown that the concentration of Zn in haulm was significantly higher in the plants which received biochar 10 t ha^{-1} (102.67 mg kg^{-1}) and the lowest was in control plots (70.50 mg kg^{-1}). It was further noticed that the treatments soil test based POP + biochar and soil test based POP were on par with the control (Table 76).

Zinc content of tuber was found to be the highest in the treatment soil test based POP (43.60 mg kg^{-1}), which was on par with soil test based POP + biochar (39.50 mg kg^{-1}). The lowest value was registered in control (28.67 mg kg^{-1}). The effect of all other treatments on this parameter was comparable.

The simple correlation studies showed that among soil properties, the Zn content (tuber) was positively correlated with electrical conductivity, organic carbon, CEC, MBC, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg and $CaCl_2$-S (Table 65).

The stepwise regression analysis with all soil properties that correlated with Zn content (Tuber) revealed that 50.9 per cent variation in this parameter could be significantly controlled by MBC and Bray-P (Table 66).

Table 76. Effect of biochar application on zinc content and uptake of Chinese potato

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	70.50	28.67	0.125	0.102	0.227
FYM 10 t ha^{-1}	82.17	32.67	0.205	0.140	0.344
Biochar 5 t ha^{-1}	87.67	34.17	0.231	0.147	0.379
Biochar 7.5 t ha^{-1}	83.83	36.50	0.225	0.154	0.379
Biochar 10 t ha^{-1}	102.67	38.33	0.274	0.170	0.443
Soil test based POP + biochar 10 t ha^{-1}	79.50	39.50	0.225	0.184	0.408
Soil test based POP	74.50	43.67	0.221	0.193	0.414
CD (0.05)	**10.89**	**4.70**	**0.033**	**0.021**	**0.042**

4.5.2.3.18. Zinc uptake

The uptake of Zn was found to be significantly influenced by the treatments. Significantly higher Zn uptake by haulm was recorded in biochar 10 t ha^{-1} (0.274 kg ha^{-1}). All other treatments had only comparable effect on this parameter (Table 76).

With respect to the Zn uptake by tuber, the treatment soil test based POP registered highest value of 0.193 kg ha^{-1}, which was on par with soil test based POP + biochar (0.184 kg ha^{-1}).

Total Zn uptake by plants was found to be the highest in the treatment biochar 10 t ha^{-1}, followed by soil test based POP and soil test based POP + biochar application which were all comparable. Significantly lowest Zn uptake by haulm, tuber and thus the total was recorded in control plots.

From the simple correlation studies, it was seen that the total Zn uptake had a positive relationship with soil properties *viz.* pH, organic carbon, CEC, MBC, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Ca, HCl-Mn and hot water soluble boron (Table 67).

The stepwise regression analysis including soil properties that correlated with total Zn uptake revealed that 60.2 per cent variation in this parameter could be controlled by the MBC content in soil. Further with successive addition of independent variables *viz.* NH_4OAc-K and Bray-P, predictability of the equation increased to 81.6 per cent (Table 68).

4.5.2.3.19. Copper content

It was seen from Table 77 that the concentration of Cu in haulm was higher in the treatments biochar 10 t ha^{-1}, biochar 7.5 t ha^{-1} and biochar 5 t ha^{-1} which were all comparable but superior to the other treatments.

With respect to the tuber, the treatment soil test based POP registered significantly higher concentration with Cu (30.17 mg kg^{-1}). This was followed by soil test based POP + biochar and biochar 10 t ha^{-1} application and the difference was significant. As could be anticipated, significantly lowest copper content in both haulm (26.83 mg kg^{-1}) and tuber (22.83 mg kg^{-1}) was associated with control plots.

Significant and positive correlation was obtained between the concentration of Cu in tuber and electrical conductivity, organic carbon, CEC, MBC, Bray-P, NH_4OAc-Ca, NH_4OAc-Mg and $CaCl_2$-S of soil (Table 65).

The stepwise regression analysis including soil properties that correlated with Cu content in tuber had shown that the variation in this parameter could be significantly altered by the soil properties *viz*. Bray-P and MBC, to the extent of 67.8 per cent (Table 66).

Table 77. Effect of biochar application on copper content and uptake of Chinese potato

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Haulm	**Tuber**	**Haulm**	**Tuber**	**Total**
Control	26.83	22.83	0.047	0.082	0.129
FYM 10 t ha^{-1}	28.00	25.67	0.070	0.110	0.179
Biochar 5 t ha^{-1}	31.50	26.17	0.083	0.113	0.196
Biochar 7.5 t ha^{-1}	31.00	25.67	0.083	0.109	0.192
Biochar 10 t ha^{-1}	32.00	27.17	0.085	0.120	0.206
Soil test based POP + biochar 10 t ha^{-1}	28.50	28.33	0.081	0.131	0.212
Soil test based POP	28.83	30.17	0.085	0.134	0.219
CD (0.05)	**1.56**	**0.79**	**0.006**	**0.005**	**0.007**

4.5.2.3.20. Copper uptake

Data in Table 77 showed that the effect of treatments biochar 5, 7.5 and 10 t ha^{-1}, soil test based POP + biochar and soil test based POP application in registering higher values with respect to the uptake of Cu by haulm was only comparable. With respect to the copper uptake by tuber, the treatments soil test based POP and soil test based POP + biochar recorded significantly higher uptake. This was followed by application of biochar at 10 t ha^{-1}, which recorded an uptake of 0.120 kg ha^{-1}.

The effect of different treatments on the total Cu uptake was similar to that of uptake by tuber. Significantly lowest uptake was registered in control (0.047, 0.082 and 0.129 kg ha^{-1} for haulm, tuber and total, respectively).

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The simple correlation analysis showed that the total Cu uptake was positively related to pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca and NH_4OAc-Mg (Table 67).

The stepwise regression analysis including the soil properties that correlated with total Cu uptake had shown that the variation in copper uptake could be attributed to the MBC and CEC of soil ($R^2 = 0.786^{**}$) (Table 68).

4.5.2.3.21. Boron content

The concentration of B in haulm and tuber of Chinese potato varied significantly among treatments (Table 78). In haulm, higher concentration of B was recorded in control, followed by application of FYM 10 t ha^{-1} and biochar 5 t ha^{-1}. The difference was also significant. Lowest B content was registered in soil test based POP (49.50 mg kg^{-1}).

The trend was reverse in the case of boron concentration in tuber, wherein the treatments soil test based POP + biochar (31.33 mg kg^{-1}), soil test based POP (33.17 mg kg^{-1}) and biochar 10 t ha^{-1} (31.00 mg kg^{-1}) recorded higher values and the control which recorded higher value in haulm (88.93 mg kg^{-1}) registered the lowest value in case of tuber (24.20 mg kg^{-1}).

Boron content of tuber was positively correlated with soil properties *viz*. pH, electrical conductivity, CEC, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Ca and NH_4OAc-Mg (Table 65).

Stepwise regression analysis between soil properties that correlated with B content (tuber) had shown that the variation in this parameter could be accounted to soil properties *viz*. Bray-P and NH_4OAc-K ($R^2 = 0.546^{**}$) (Table 66).

4.5.2.3.22. Boron uptake

Uptake of B by haulm was found to be higher in the treatments which consisted of FYM 10 t ha^{-1} (0.209 kg ha^{-1}) and biochar 5 t ha^{-1} (0.198 kg ha^{-1}). This was followed by application of biochar 7.5 t ha^{-1} and biochar 10 t ha^{-1}, which was on par with soil test based POP + biochar application (Table 78).

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With respect to the uptake of B by tuber, the higher values were recorded in soil test based POP + biochar application, which was on par with biochar 10 t ha^{-1} and soil test based POP application. All other treatments showed a comparable effect on this parameter and significantly lowest value was registered in control (0.086 kg ha^{-1}).

Total B uptake by plants was higher in the treatment FYM 10 t ha^{-1} (0.317 kg ha^{-1}) and it was on par with biochar 5 t ha^{-1} (0.304 kg ha^{-1}). This was followed by the treatments biochar 10 t ha^{-1} and soil test based POP + biochar. Significantly lowest value was registered by control plots (0.243 kg ha^{-1}).

The simple correlation studies revealed the positive and significant relationship of total B uptake with organic carbon, MBC, dehydrogenase activity, $KMnO_4$-N, NH_4OAc-Mg, HCl-Zn and HCl-Cu (Table 67).

The stepwise regression analysis in view of all the soil properties that correlated with total B uptake revealed that 51.4 per cent variability in this parameter could be attributed to MBC. Further, predictability of the equation could be increased with successive inclusion of HCl-Cu and NH_4OAc-Mg content of soil ($R^2 = 0.777^{**}$) (Table 68).

Table 78. Effect of biochar application on boron content and uptake of Chinese potato

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Haulm	Tuber	Haulm	Tuber	Total
Control	88.93	24.20	0.157	0.086	0.243
FYM 10 t ha^{-1}	83.83	25.33	0.209	0.109	0.317
Biochar 5 t ha^{-1}	75.17	24.50	0.198	0.106	0.304
Biochar 7.5 t ha^{-1}	63.17	26.50	0.169	0.112	0.281
Biochar 10 t ha^{-1}	61.50	31.00	0.164	0.137	0.301
Soil test based POP + biochar 10 t ha^{-1}	55.00	31.33	0.156	0.145	0.301
Soil test based POP	49.50	31.17	0.146	0.138	0.285
CD (0.05)	**4.16**	**2.07**	**0.014**	**0.010**	**0.014**

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4.5.3. Residual effect of biochar on cowpea

4.5.3.1. Growth parameters and yield

Plant height

Perusal of data in Table 79 revealed that the treatments had significant influence on the plant height. Significantly the highest plant height was recorded in the treatment soil test based POP + biochar application (39.74 cm). This was followed by the treatments FYM 10 t ha^{-1} (37.50 cm), soil test based POP (37.48 cm) and biochar 7.5 t ha^{-1} (37.05 cm) which were on par with each other. Significantly lowest plant height was observed in the plants grown under control (31.51 cm).

The plant height had a positive relationship with pod length, number of pods per plant, DMP and yield, whereas the crude fibre content had a negative relationship with the plant height (Table 80). With respect to the soil properties, plant height had positive relationship with pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Zn and hot water soluble B (Table 81).

Further, the stepwise regression analysis making use of all soil properties that correlated with plant height revealed that 74.1 per cent variation in plant height could be explained by dehydrogenase activity and Bray-P of soil (Table 82).

Table 79. Effect of biochar application on growth and yield of cowpea (residual crop)

Treatments	**Plant height (cm)**	**Pod length (cm)**	**No. of pods per plant**	**DMP (kg ha^{-1})**	**Pod yield (t ha^{-1})**
Control	31.51	13.33	8.83	1166.5	4.720
FYM 10 t ha^{-1}	37.50	14.33	11.50	1407.8	5.859
Biochar 5 t ha^{-1}	34.92	13.99	12.67	1193.5	5.793
Biochar 7.5 t ha^{-1}	37.05	14.36	13.17	1438.6	6.194
Biochar 10 t ha^{-1}	34.33	14.55	11.17	1195.8	6.088
Soil test based POP + biochar 10 t ha^{-1}	39.74	15.27	14.17	1463.5	6.624
Soil test based POP	37.48	15.10	12.83	1472.6	5.806
CD (0.05)	**2.25**	**0.42**	**1.42**	**108.6**	**0.559**

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Table 80. Correlation analysis among the growth, yield and quality attributes of cowpea (n = 21)

Parameters	Plant height	Pod length	Pods per plant	DMP	Yield	Protein	Crude fibre
Plant height	1.000						
Pod length	0.704**	1.000					
Pods per plant	0.844**	0.650**	1.000				
DMP	0.819**	0.675**	0.609**	1.000			
Yield	0.689**	0.724**	0.708**	0.577**	1.000		
Protein	0.160^{NS}	0.110^{NS}	0.123^{NS}	0.158^{NS}	0.361^{NS}	1.000	
Crude fibre	-0.469*	-0.572**	-0.625**	-0.231^{NS}	-0.742**	-0.460*	1.000

Table 81. Correlation analysis between the growth, yield and quality attributes of cowpea and the post-harvest soil properties (n = 21)

Parameters		Plant height	Pod length	Pods per plant	DMP	Yield	Protein	Crude fibre
pH		0.511*	0.444*	0.599**	0.210^{NS}	0.778**	0.458*	-0.737**
EC		0.262^{NS}	0.276^{NS}	0.142^{NS}	0.275^{NS}	-0.069^{NS}	-0.257^{NS}	-0.035^{NS}
OC		0.667**	0.566**	0.769**	0.336^{NS}	0.756**	0.341^{NS}	-0.788**
CEC		0.599**	0.620**	0.620**	0.283^{NS}	0.729**	0.371^{NS}	-0.759**
MBC		0.436*	0.589**	0.614**	0.270^{NS}	0.362^{NS}	0.043^{NS}	-0.479*
DHY		0.801**	0.802**	0.682**	0.598**	0.685**	-0.139^{NS}	-0.399^{NS}
Available nutrient status	**N**	0.652**	0.592**	0.700**	0.566**	0.585**	-0.237^{NS}	-0.414^{NS}
	P	0.733**	0.777**	0.585**	0.806**	0.594**	0.135^{NS}	-0.434*
	K	0.117^{NS}	0.228^{NS}	0.313^{NS}	-0.107^{NS}	0.540*	0.479*	-0.670**
	Ca	0.240^{NS}	0.292^{NS}	0.369^{NS}	0.011^{NS}	0.548*	0.427^{NS}	-0.679**
	Mg	0.319^{NS}	0.149^{NS}	0.463*	0.266^{NS}	0.522*	0.476*	-0.551**
	S	0.581**	0.507*	0.600**	0.443*	0.283^{NS}	-0.309^{NS}	-0.263^{NS}
	Fe	0.301^{NS}	0.309^{NS}	0.361^{NS}	0.202^{NS}	0.318^{NS}	0.020^{NS}	-0.260^{NS}
	Mn	-0.132^{NS}	-0.324^{NS}	-0.437*	0.098^{NS}	-0.525*	-0.303^{NS}	0.697**
	Zn	0.738**	0.777**	0.572**	0.592**	0.693**	0.233^{NS}	-0.492*
	Cu	0.158^{NS}	0.364^{NS}	0.325^{NS}	0.170^{NS}	0.513*	0.318^{NS}	-0.542*
	B	0.623**	0.564**	0.744**	0.541*	0.745**	0.330^{NS}	-0.682**

Table 82. Stepwise regression analysis between the growth and quality attributes of cowpea and post-harvest soil properties

Y	R^2	Regression equation
Plant height	0.642^{**}	Y = 29.208 + 0.069(Dehydrogenase)
	0.741^{**}	Y = 25.152 + 0.048(Dehydrogenase) + 0.137(P)
Pod length	0.644^{**}	Y = 12.786 + 0.016(Dehydrogenase)
	0.780^{**}	Y = 11.659 + 0.011(Dehydrogenase) + 0.038(P)
No. of Pods per plant	0.590^{**}	Y = -16.51 + 16.043(OC)
	0.699^{**}	Y = -25.36 + 11.468(OC) + 0.092(N)
	0.779^{**}	Y = -18.112 + 5.597(OC) + 0.093(N) + 18.384(P)
	0.750^{**}	Y = -13.140 + 0.114(N) + 25.532(B)
	0.837^{**}	Y = 1.627 – 0.007(N) + 32.614(B) + 0.883(S)
	0.836^{**}	Y = 0.691 + 32.18(B) + 0.846(S)
DMP	0.649^{**}	Y = 691.261 + 14.462(P)
Protein	0.229^{**}	Y = 20.261 + 0.004(K)
Crude fibre	0.625^{**}	Y = 42.147 – 15.211(OC)
	0.714^{**}	Y = 30.103 – 11.201(OC) + 0.056(Mn)

Pod length

It is clear from the data (Table 79) that the application of different treatments had significant residual effect on pod length. The plants that received soil test based POP + biochar and soil test based POP produced pods with greater length which were on par with each other, but superior to rest of the treatments. Significantly the lowest pod length was recorded in control. Residual effect of all other treatments was comparable.

The simple correlation studies unveiled the positive and significant relationship of pod length with plant height, number of pods per plant, DMP, pod yield and crude fibre content (Table 80). It was also noticed that the pod length was positively correlated with the soil properties *viz.* pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Zn and hot water soluble boron (Table 81).

As seen in case of plant height, the stepwise regression analysis had shown that the variability in the pod length could be attributed to dehydrogenase activity and Bray-P status of soil ($R^2 = 0.780^{**}$) (Table 82).

Number of pods per plant

Number of pods per plant was found to be the highest in the treatment soil test based POP + biochar (14.17). However, it was on par with biochar 7.5 t ha^{-1} and soil test based POP application. Significantly lowest number of pods per plant was registered in control (Table 79).

Through the simple correlation studies, a positive and significant relationship was noticed between the number of pods per plant and plant height, pod length, DMP and pod yield, whereas the relationship with crude fibre was negative (Table 80). It was further made out that the number of pods per plant was positively related with the soil properties *viz.* pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-Mg, $CaCl_2$-S, HCl-Zn and hot water soluble B, whereas negatively with HCl-Mn (Table 81).

Stepwise regression analysis including soil properties that correlated with number of pods per plant had shown that the organic carbon content contributed to this parameter to the extent of 59.0 per cent and with further inclusion of $KMnO_4$-N and Bray-P, predictability of the equation could be improved to 77.9 per cent. Furthermore, stepwise regression analysis yielded an equation with 83.7 per cent predictability by inclusion of $KMnO_4$-N, hot water soluble B and $CaCl_2$-S (Table 82).

Dry matter production

Dry matter production was found to be greater for the treatments *viz.* soil test based POP, soil test based POP + biochar, biochar 7.5 t ha^{-1} and FYM 10 t ha^{-1} application which were all comparable. The lowest DMP of 1166.5 kg ha^{-1} was recorded in the control plots (Table 79).

Dry matter production had a significant positive correlation with plant height, pod length, number of pods per plant and yield (Table 80). Among the soil properties, it had positive correlation with dehydrogenase activity, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Zn and hot water soluble B (Table 81).

Stepwise regression analysis with soil properties that correlated with the DMP had shown that, 64.9 per cent variability in this parameter could be attributed to the Bray-P status of soil (Table 82).

Pod yield

The fresh pod yield of cowpea as influenced by different treatments is presented in Table 79. It was seen from the results that the higher pod yield was recorded in the plots that received soil test based POP + biochar (6.624 t ha^{-1}), though it was comparable with biochar 7.5 t ha^{-1} (6.194 t ha^{-1}) and biochar 10 t ha^{-1} (6.088 t ha^{-1}). As could be anticipated, the lowest pod yield was recorded in the control plots. The residual effect of all other treatments on pod yield was comparable but superior to the control plots.

The simple correlation studies unveiled the positive and significant relationship of pod yield with plant height, pod length, number of pods per plant and DMP (Table 80). It was further observed that the pod yield was positively related with the soil properties *viz.* pH, organic carbon, CEC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, whereas negatively with the HCl-Mn content (Table 81).

Path analysis

Path coefficients of growth components indicating the direct and indirect effect on pod yield is given in Table 83. The direct effect of pod length (0.435) and pods per plant (0.357) on pod yield was very high and positive, whereas the direct effect of pH and DMP was only negligible. Indirect effect of pH through pod length (0.306) and pods per plant (0.301) was high and positive. Indirect effect of DMP through pod length (0.294) and pods per plant (0.217) was moderate and positive.

The direct and indirect effect of content of nutrients in pod on pod yield as indicated by path coefficients are given in Table 84. The direct effect of P (0.169) and Ca (0.171) was moderate and positive, whereas the direct effect of K and Zn was low and positive. The direct effect of Fe and Mn was moderate but negative.

Table 83. Path coefficients of growth parameters to the pod yield

	Plant height	Pod length	Pods per plant	DMP	Correlation coefficient
Plant height	**0.083**	0.306	0.301	-0.001	0.689
Pod length	0.058	**0.435**	0.232	-0.001	0.724
Pods per plant	0.070	0.283	**0.357**	-0.001	0.708
DMP	0.068	0.294	0.217	**-0.001**	0.577

Table 84. Path coefficients of nutrient content of pod to the pod yield

	P	K	Ca	Fe	Mn	Zn	Correlation coefficient
P	**0.169**	0.041	0.031	0.145	0.150	0.045	0.581
K	0.066	**0.105**	0.103	0.095	0.049	0.066	0.484
Ca	0.031	0.064	**0.171**	0.143	0.063	0.082	0.554
Fe	-0.083	-0.034	-0.082	**-0.297**	-0.184	-0.093	-0.773
Mn	-0.113	-0.023	-0.048	-0.244	**-0.224**	-0.085	-0.737
Zn	0.063	0.057	0.116	0.229	0.157	**0.121**	0.743

Table 85. Path coefficients of nutrient content of shoot to the pod yield

	N	P	K	Mg	S	Fe	Mn	Zn	B	Correlation coefficient
N	**0.244**	-0.159	0.049	0.087	0.199	0.100	0.072	0.034	-0.005	0.622
P	0.122	**-0.317**	0.033	0.111	0.173	0.330	0.106	0.049	-0.052	0.555
K	0.075	-0.065	**0.161**	0.032	0.022	0.179	0.260	0.035	-0.093	0.606
Mg	0.127	-0.210	0.031	**0.168**	0.239	0.182	0.099	0.037	-0.040	0.632
S	0.144	-0.162	0.011	0.119	**0.338**	0.162	0.074	0.027	-0.043	0.670
Fe	-0.060	0.257	-0.071	-0.075	-0.135	**-0.408**	-0.197	-0.044	0.097	-0.635
Mn	-0.059	0.113	-0.141	-0.056	-0.084	-0.270	**-0.297**	-0.038	0.112	-0.720
Zn	-0.129	0.243	-0.088	-0.097	-0.144	-0.285	-0.178	**-0.063**	0.089	-0.652
B	0.008	-0.106	0.097	0.044	0.093	0.256	0.215	0.037	**-0.155**	0.488

Table 86. Path coefficients of post-harvest soil properties and available nutrient status to the pod yield

	pH	OC	CEC	DHY	N	P	K	Ca	Mg	Mn	Zn	Cu	B	Correlation coefficient
pH	**1.554**	-0.605	0.313	-0.115	0.158	-0.123	-0.669	0.076	-0.405	-0.181	0.017	0.296	0.463	0.778
OC	1.290	**-0.729**	0.318	-0.145	0.322	-0.167	-0.481	0.078	-0.353	-0.145	0.015	0.275	0.477	0.756
CEC	1.201	-0.573	**0.405**	-0.158	0.159	-0.187	-0.613	0.081	-0.286	-0.157	0.019	0.326	0.513	0.729
DHY	0.683	-0.404	0.245	**-0.262**	0.372	-0.212	-0.086	0.018	-0.005	-0.063	0.019	0.070	0.310	0.685
N	0.423	-0.404	0.111	-0.167	**0.581**	-0.186	0.078	0.012	-0.104	-0.042	0.011	0.013	0.259	0.585
P	0.540	-0.345	0.214	-0.157	0.306	**-0.353**	-0.137	0.033	-0.192	-0.022	0.021	0.234	0.452	0.594
K	1.258	-0.424	0.301	-0.027	-0.055	-0.058	**-0.826**	0.086	-0.367	-0.204	0.010	0.420	0.427	0.540
Ca	1.102	-0.530	0.307	-0.044	0.066	-0.108	-0.659	**0.107**	-0.399	-0.153	0.008	0.388	0.464	0.548
Mg	1.054	-0.431	0.194	-0.002	0.101	-0.113	-0.507	0.072	**-0.597**	-0.106	0.007	0.326	0.526	0.522
Mn	-1.124	0.422	-0.255	0.066	-0.097	0.032	0.675	-0.066	0.254	**0.250**	-0.008	-0.322	-0.351	-0.525
Zn	0.964	-0.418	0.291	-0.190	0.245	-0.276	-0.314	0.032	-0.156	-0.074	**0.027**	0.165	0.398	0.693
Cu	0.834	-0.364	0.239	-0.033	0.013	-0.150	-0.629	0.075	-0.353	-0.146	0.008	**0.551**	0.466	0.513
B	1.075	-0.520	0.311	-0.121	0.225	-0.238	-0.527	0.074	-0.470	-0.131	0.016	0.384	**0.669**	0.745

With respect to the direct and indirect effects of concentration of nutrients in shoot on pod yield, the path coefficients obtained are presented in Table 85. The direct effect of N (0.244), K (0.161), Mg (0.168) was moderate and positive, whereas the direct effect of S was high and positive. Direct effect of P, Fe and Mn on pod yield was high (-0.317), very high (-0.408) and moderate (-0.297), respectively but the effect was negative.

Path coefficients explaining the direct as well as the indirect effects of different soil properties on pod yield are presented in Table 86. The direct effect of pH, CEC, $KMnO_4$-N, HCl-Cu and hot water soluble B was very high and positive and the direct effect of NH_4OAc-Ca was low and positive. The direct effect of organic carbon, dehydrogenase activity, Bray-P, NH_4OAc-K and NH_4OAc-Mg was high but negative.

4.5.3.2. Quality attributes of cowpea pods

Protein

Data on the residual effect of treatments on protein content of cowpea pod is presented in Table 87. Protein content was found to be higher for the treatment biochar 10 t ha^{-1} (22.75 %), though it was comparable with biochar 7.5 t ha^{-1} (22.43 %), FYM 10 t ha^{-1} (22.11 %) and soil test based POP application (21.93 %). The lowest protein content was recorded in control (21.08 %) and soil test based POP + biochar (21.11 %) which were comparable.

From the simple correlation studies it could be concluded that, the protein content was positively related to the concentration of N and P in pods (Table 88)

Stepwise regression analysis considering soil properties that correlated with protein content had shown that the variation in this parameter could be attributed to the NH_4OAc-K content of soil ($R^2 = 0.229^{**}$) (Table 82). In addition, the stepwise regression analysis between the nutrient content of pods and protein revealed that 100 per cent variation in the protein content could be significantly explained by the concentration of N in pods.

$$\text{Protein} = 0.023 + 6.244(\text{N})\ (R^2=1.000^{**})$$

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Table 87. Effect of biochar application on quality attributes of cowpea pods

Treatments	Crude protein	Crude fibre
	%	
Control	21.08	18.17
FYM 10 t ha^{-1}	22.11	15.67
Biochar 5 t ha^{-1}	21.57	14.17
Biochar 7.5 t ha^{-1}	22.43	14.50
Biochar 10 t ha^{-1}	22.75	13.67
Soil test based POP + biochar 10 t ha^{-1}	21.11	14.17
Soil test based POP	21.93	15.17
CD (0.05)	**0.89**	**1.31**

Table 88. Correlation analysis between the nutrient content of pod and quality attributes of cowpea

Parameters		Crude Protein	Crude fibre
Nutrient content of pod	**N**	1.000**	-0.464*
	P	0.480*	-0.404^{NS}
	K	0.354^{NS}	-0.577**
	Ca	0.263^{NS}	-0.580**
	Mg	0.255^{NS}	-0.231^{NS}
	S	0.190^{NS}	-0.094^{NS}
	Fe	-0.320^{NS}	0.731**
	Mn	-0.401^{NS}	0.618**
	Zn	0.342^{NS}	-0.821**
	Cu	0.299^{NS}	-0.353^{NS}
	B	0.433^{NS}	-0.298^{NS}

Crude fibre

The crude fibre content of cowpea pods varied significantly among the treatments (Table 87). Significantly highest crude fibre content was recorded in the cowpea pods harvested from the control plots (18.17 %). This was followed by the treatment FYM 10 t ha^{-1} which recorded 15.67 per cent crude fibre. The residual effect of all other treatments on this parameter was only marginal. However, the lowest crude fibre content was associated with the application of biochar 10 t ha^{-1} (13.67 %).

The simple correlation studies showed that the crude fibre content was positively related with Fe and Mn content of pods and negatively with N, K, Ca and Zn content of pods (Table 88). Among the soil properties, crude fibre had negative correlation with pH, organic carbon, CEC, MBC, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, whereas correlation was positive with HCl-Mn (Table 81).

The stepwise regression including soil properties that correlated with crude fibre content had shown that 71.4 per cent variability in this parameter could be attributed to the organic carbon and HCl-Mn status of soil (Table 82). In addition, the stepwise regression analysis between the nutrient content of pod and crude fibre revealed that the variation in crude fibre content of pods could be attributed to the concentration of Zn in pods ($R^2 = 0.674^{**}$).

$$\text{Crude fibre} = 24.84 - 0.163(\text{Zn}) \ (R^2 = 0.674^{**})$$

4.5.3.3. Nutrient content and uptake

4.5.3.3.1. Nitrogen content

The data on N content of shoot and pod is given in Table 89. The highest content of N in shoot was noticed with the application of FYM 10 t ha^{-1}. However, it was on par with the treatments biochar 7.5 t ha^{-1}, biochar 10 t ha^{-1}, soil test based POP + biochar and soil test based POP application. Lowest value was recorded in control (1.725 %) and biochar 5 t ha^{-1} (1.75 %).

As regards the N content in pod, the highest value was recorded by biochar 10 t ha^{-1} (3.64 %) which was comparable with biochar 7.5 t ha^{-1}, FYM 10 t ha^{-1} and soil test based POP application. The lowest value of 3.372 per cent was registered in control which was comparable with soil test based POP + biochar application (3.377 %).

Nitrogen content in pod had significant positive correlation with pH, NH_4OAc-K, NH_4OAc-Ca and NH_4OAc-Mg (Table 90).

The stepwise regression analysis including soil properties that correlated with the N content in pod revealed that the variation in this parameter could be significantly explained by NH_4OAc-K ($R^2 = 0.229^{**}$) (Table 91).

4.5.3.3.2. Nitrogen uptake

Perusal of data in Table 89 revealed that the highest uptake of N by shoot was registered by the treatments soil test based POP + biochar (32.11 kg ha^{-1}), soil test based POP (31.62 kg ha^{-1}), FYM 10 t ha^{-1} (31.49 kg ha^{-1}) and biochar 7.5 t ha^{-1} (30.62 kg ha^{-1}). Lowest was in the control plots (20.12 kg ha^{-1}).

In case of N uptake by pod, application of soil test based POP + biochar registered higher value of 30.29 kg ha^{-1} and it was followed by biochar 7.5 t ha^{-1} (28.34 kg ha^{-1}). Significantly lower uptake was in control. All other treatments had comparable residual effect on this parameter.

With respect to the total N uptake by plant, the treatment soil test based POP + biochar recorded highest uptake of 62.40 kg ha^{-1} though it was comparable with biochar 7.5 t ha^{-1} (58.96 kg ha^{-1}) and soil test based POP application (57.87 kg ha^{-1}). Significantly lowest uptake was in control plots.

Total N uptake had significant positive correlation with soil properties *viz.* pH, organic carbon, CEC, dehydrogenase activity, $KMnO_4$-N, Bray-P, HCl-Zn and hot water soluble B (Table 92).

Around 77.5 per cent variation in the total N uptake could be significantly explained through stepwise regression analysis with successive addition of the independent variables *viz.* Bray-P and dehydrogenase activity (Table 93).

Table 89. Effect of biochar application on nitrogen content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	1.725	3.372	20.12	17.88	38.01
FYM 10 t ha^{-1}	2.225	3.537	31.49	24.56	56.05
Biochar 5 t ha^{-1}	1.75	3.451	20.88	24.12	45.00
Biochar 7.5 t ha^{-1}	2.128	3.589	30.62	28.34	58.96
Biochar 10 t ha^{-1}	2.053	3.640	24.54	25.15	49.69
Soil test based POP + biochar 10 t ha^{-1}	2.194	3.377	32.11	30.29	62.40
Soil test based POP	2.147	3.509	31.62	26.24	57.87
CD (0.05)	**0.253**	**0.143**	**4.89**	**2.66**	**6.23**

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Table 90. Correlation analysis between the nutrient content of pod and the post-harvest soil properties (n = 21)

Parameters		Nutrient content of pod										
		N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH		0.462^{*}	0.648^{**}	0.681^{**}	0.595^{**}	0.337^{NS}	0.283^{NS}	-0.648^{**}	-0.664^{**}	0.813^{**}	0.369^{NS}	0.467^{*}
EC		-0.263^{NS}	-0.180^{NS}	0.039^{NS}	-0.268^{NS}	0.199^{NS}	-0.230^{NS}	-0.152^{NS}	0.120^{NS}	-0.221^{NS}	-0.056^{NS}	-0.123^{NS}
OC		0.344^{NS}	0.530^{*}	0.530^{*}	0.698^{**}	0.376^{NS}	0.045^{NS}	-0.780^{**}	-0.596^{**}	0.850^{**}	0.431^{NS}	0.345^{NS}
CEC		0.377^{NS}	0.604^{**}	0.379^{NS}	0.468^{*}	0.002^{NS}	-0.163^{NS}	-0.747^{**}	-0.835^{**}	0.854^{**}	0.057^{NS}	0.041^{NS}
MBC		0.045^{NS}	0.112^{NS}	0.218^{NS}	0.410^{NS}	0.270^{NS}	-0.308^{NS}	-0.785^{**}	-0.349^{NS}	0.507^{*}	0.285^{NS}	0.067^{NS}
DHY		-0.139^{NS}	0.492^{*}	0.080^{NS}	0.122^{NS}	-0.092^{NS}	-0.501^{*}	-0.691^{**}	-0.664^{**}	0.460^{*}	-0.213^{NS}	-0.341^{NS}
Available nutrient status	N	-0.239^{NS}	0.137^{NS}	0.254^{NS}	0.426^{NS}	0.301^{NS}	-0.162^{NS}	-0.577^{**}	-0.213^{NS}	0.366^{NS}	0.229^{NS}	0.061^{NS}
	P	0.135^{NS}	0.605^{**}	0.269^{NS}	0.291^{NS}	0.196^{NS}	-0.486^{*}	-0.670^{**}	-0.672^{**}	0.428^{NS}	-0.023^{NS}	0.018^{NS}
	K	0.486^{*}	0.358^{NS}	0.537^{*}	0.541^{*}	0.028^{NS}	0.304^{NS}	-0.491^{*}	-0.609^{**}	0.762^{**}	0.261^{NS}	0.353^{NS}
	Ca	0.434^{*}	0.354^{NS}	0.509^{*}	0.681^{**}	0.196^{NS}	0.138^{NS}	-0.540^{*}	-0.519^{*}	0.819^{**}	0.451^{*}	0.399^{NS}
	Mg	0.478^{*}	0.489^{*}	0.718^{**}	0.842^{**}	0.489^{*}	0.420^{NS}	-0.357^{NS}	-0.326^{NS}	0.578^{**}	0.759^{**}	0.672^{**}
	S	-0.311^{NS}	-0.012^{NS}	0.140^{NS}	0.163^{NS}	0.311^{NS}	-0.182^{NS}	-0.414^{NS}	-0.054^{NS}	0.188^{NS}	0.135^{NS}	-0.034^{NS}
	Fe	0.027^{NS}	0.004^{NS}	-0.189^{NS}	0.166^{NS}	-0.421^{NS}	-0.370^{NS}	-0.357^{NS}	-0.343^{NS}	0.333^{NS}	-0.210^{NS}	-0.459^{*}
	Mn	-0.309^{NS}	-0.182^{NS}	-0.347^{NS}	-0.517^{*}	0.136^{NS}	-0.201^{NS}	0.603^{**}	0.565^{**}	-0.696^{**}	-0.192^{NS}	-0.117^{NS}
	Zn	0.233^{NS}	0.781^{**}	0.366^{NS}	0.156^{NS}	0.191^{NS}	-0.321^{NS}	-0.732^{**}	-0.837^{**}	0.552^{**}	-0.160^{NS}	0.026^{NS}
	Cu	0.327^{NS}	0.284^{NS}	0.233^{NS}	0.574^{**}	-0.084^{NS}	0.017^{NS}	-0.529^{*}	-0.595^{**}	0.631^{**}	0.210^{NS}	0.192^{NS}
	B	0.333^{NS}	0.552^{**}	0.573^{**}	0.791^{**}	0.173^{NS}	-0.055^{NS}	-0.677^{**}	-0.698^{**}	0.757^{**}	0.407^{NS}	0.248^{NS}

Table 91. Stepwise regression analysis between the nutrient content of pod and post-harvest soil properties

Y	R^2	Regression equation
N	0.229^{**}	Y = 3.242 + 0.001(K)
P	0.651^{**}	Y = 0.043 + 0.031(Zn)
	0.732^{**}	Y = -0.001 + 0.028(Zn) + 0.001(Mg)
K	0.520^{**}	Y = 0.966 + 0.012(Mg)
Ca	0.698^{**}	Y = -0.037 + 0.005(Mg)
Mg	0.214^{**}	Y = 0.043 + 0.002(Mg)
S	0.327^{**}	Y = 0.086 + 0.0001(Dehydrogenase)
Fe	0.617^{**}	Y = 912.971 – 4.027(MBC)
	0.874^{**}	Y = 1430.349 – 3.020(MBC) – 143.068(CEC)
	0.902^{**}	Y = 1370.441 – 2.793(MBC) – 118.996(CEC) – 2.076(P)
Mn	0.700^{**}	Y = 291.338 – 34.837(Zn)
	0.830^{**}	Y = 403.063 – 30.120(Zn) – 58.733(Cu)
Zn	0.731^{**}	Y = -49.435 + 23.716(CEC)
	0.814^{**}	Y = -82.954 + 13.561(CEC) + 45.126(OC)
Cu	0.576^{**}	Y = -9.413 + 0.268(Mg)
	0.581^{**}	Y = -6.133 + 0.292(Mg) – 0.014(Ca)
B	0.452^{**}	Y = -24.136 + 0.606(Mg)
	0.610^{**}	Y = 31.081 + 0.572(Mg) – 2.645(Fe)

4.5.3.3.3. Phosphorus content

Concentration of P in shoot and pod of plants receiving different treatments is presented in Table 94. In both shoot and pod, the concentration of P was found to be maximum in the plants that received FYM 10 t ha^{-1}. However, it was on par with the treatments biochar 7.5 t ha^{-1} and biochar 5 t ha^{-1} in case of shoot, and with application of biochar 7.5 t ha^{-1}, biochar 10 t ha^{-1} and soil test based POP + biochar in case of pod. Lowest value was recorded in control.

The simple correlation studies made clear the positive and significant relationship of P content (pod) with pH, organic carbon, CEC, dehydrogenase activity, Bray-P, NH_4OAc-Mg, HCl-Zn and hot water soluble B (Table 90).

Furthermore, the stepwise regression analysis including soil properties that correlated with P content (pod) revealed that, variation in the content of P in pod could be attributed to the HCl-Zn and NH_4OAc-Mg of soil ($R^2 = 0.732^{**}$) (Table 91).

Table 92. Correlation analysis between the nutrient uptake by cowpea and the post-harvest soil properties (n = 21)

Parameters		Total nutrient uptake										
		N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B
pH		0.513^{*}	0.646^{**}	0.736^{**}	0.305^{NS}	0.431^{NS}	0.548^{*}	-0.585^{**}	-0.636^{**}	0.259^{NS}	0.802^{**}	0.743^{**}
EC		0.163^{NS}	0.105^{NS}	-0.082^{NS}	0.386^{NS}	0.400^{NS}	0.138^{NS}	0.347^{NS}	0.432^{NS}	-0.149^{NS}	0.008^{NS}	-0.010^{NS}
OC		0.563^{**}	0.725^{**}	0.718^{**}	0.514^{*}	0.626^{**}	0.507^{*}	-0.611^{**}	-0.553^{**}	0.263^{NS}	0.752^{**}	0.835^{**}
CEC		0.555^{**}	0.593^{**}	0.868^{**}	0.287^{NS}	0.430^{NS}	0.293^{NS}	-0.441^{*}	-0.728^{**}	0.447^{*}	0.596^{**}	0.623^{**}
MBC		0.361^{NS}	0.477^{*}	0.358^{NS}	0.566^{**}	0.555^{**}	0.207^{NS}	-0.406^{NS}	-0.256^{NS}	-0.128^{NS}	0.487^{*}	0.488^{*}
DHY		0.714^{**}	0.687^{**}	0.735^{**}	0.510^{*}	0.711^{**}	0.410^{NS}	0.182^{NS}	-0.194^{NS}	0.637^{**}	0.381^{NS}	0.409^{NS}
Available nutrient status	**N**	0.599^{**}	0.655^{**}	0.474^{*}	0.650^{**}	0.817^{**}	0.578^{**}	-0.059^{NS}	0.025^{NS}	0.453^{*}	0.474^{*}	0.575^{**}
	P	0.840^{**}	0.783^{**}	0.783^{**}	0.735^{**}	0.736^{**}	0.433^{NS}	0.099^{NS}	-0.042^{NS}	0.469^{*}	0.514^{*}	0.565^{**}
	K	0.187^{NS}	0.254^{NS}	0.579^{**}	-0.036^{NS}	-0.005^{NS}	0.213^{NS}	-0.715^{**}	-0.871^{**}	0.091^{NS}	0.604^{**}	0.515^{*}
	Ca	0.253^{NS}	0.387^{NS}	0.587^{**}	0.128^{NS}	0.178^{NS}	0.230^{NS}	-0.752^{**}	-0.749^{**}	0.165^{NS}	0.589^{**}	0.670^{**}
	Mg	0.421^{NS}	0.573^{**}	0.504^{*}	0.327^{NS}	0.339^{NS}	0.579^{**}	-0.631^{**}	-0.376^{NS}	0.240^{NS}	0.762^{**}	0.725^{**}
	S	0.399^{NS}	0.449^{*}	0.222^{NS}	0.565^{**}	0.721^{**}	0.434^{*}	0.065^{NS}	0.217^{NS}	0.220^{NS}	0.274^{NS}	0.346^{NS}
	Fe	0.296^{NS}	0.217^{NS}	0.430^{NS}	0.157^{NS}	0.223^{NS}	-0.063^{NS}	0.002^{NS}	-0.391^{NS}	0.364^{NS}	0.089^{NS}	0.095^{NS}
	Mn	-0.202^{NS}	-0.242^{NS}	-0.520^{*}	-0.047^{NS}	-0.079^{NS}	-0.193^{NS}	0.627^{**}	0.871^{**}	-0.113^{NS}	-0.566^{**}	-0.451^{*}
	Zn	0.758^{**}	0.744^{**}	0.809^{**}	0.552^{**}	0.659^{**}	0.453^{*}	0.010^{NS}	-0.227^{NS}	0.384^{NS}	0.567^{**}	0.546^{*}
	Cu	0.307^{NS}	0.329^{NS}	0.583^{**}	0.199^{NS}	0.076^{NS}	0.159^{NS}	-0.533^{*}	-0.699^{**}	0.194^{NS}	0.528^{*}	0.496^{*}
	B	0.703^{**}	0.747^{**}	0.851^{**}	0.500^{*}	0.564^{**}	0.554^{**}	-0.443^{*}	-0.518^{*}	0.561^{**}	0.771^{**}	0.767^{**}

Table 93. Stepwise regression analysis between the total nutrient uptake (cowpea) and post-harvest soil properties

Y	R^2	Regression equation
N	0.706^{**}	Y = 11.235 + 0.930(P)
	0.775^{**}	Y = 11.956 + 0.713(P) + 0.089(Dehydrogenase)
P	0.613^{**}	Y = 0.178 + 0.069(P)
	0.779^{**}	Y = -5.629 + 0.050(P) + 3.739(OC)
K	0.754^{**}	Y = -73.355 + 27.096(CEC)
	0.900^{**}	Y = -62.745 + 19.862(CEC) + 0.530(P)
	0.921^{**}	Y = -95.818 + 13.759(CEC) + 0.553(P) + 10.173(pH)
Ca	0.540^{**}	Y = 14.317 + 0.371(P)
	0.662^{**}	Y = 7.553 + 0.331(P) + 1.268(S)
Mg	0.668^{**}	Y = -17.194 + 0.126(N)
	0.797^{**}	Y = -13.663 + 0.092(N) + 0.064(P)
S	0.338^{**}	Y = -0.380 + 0.016(Mg)
	0.583^{**}	Y = -1.349 + 0.017(Mg) + 0.112(S)
Fe	0.565^{**}	Y = 3.194 – 0.005(Ca)
Mn	0.760^{**}	Y = -0.432 + 0.013(Mn)
	0.835^{**}	Y = 0.438 + 0.007(Mn) – 0.001(K)
Zn	0.394^{**}	Y = 0.077 + 0.0001(Dehydrogenase)
Cu	0.431^{**}	Y = 0.010 + 0.0001(P)
	0.610^{**}	Y = -0.008 + 0.0001(P) + 0.0001(Mg)
	0.694^{**}	Y = -0.044 + 0.0001(P) + 0.0001(Mg) + 0.0001(N)
B	0.732^{**}	Y = -0.190 + 0.171(OC)
	0.815^{**}	Y = -0.174 + 0.129(OC) + 0.001(Mg)

Table 94. Effect of biochar application on phosphorus content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	0.073	0.193	0.852	1.028	1.880
FYM 10 t ha^{-1}	0.138	0.246	1.946	1.705	3.651
Biochar 5 t ha^{-1}	0.131	0.200	1.561	1.400	2.961
Biochar 7.5 t ha^{-1}	0.135	0.238	1.939	1.880	3.819
Biochar 10 t ha^{-1}	0.108	0.235	1.296	1.623	2.919
Soil test based POP + biochar 10 t ha^{-1}	0.121	0.240	1.772	2.150	3.921
Soil test based POP	0.126	0.220	1.851	1.650	3.501
CD (0.05)	**0.013**	**0.018**	**0.247**	**0.165**	**0.320**

4.5.3.3.4. Phosphorus uptake

Uptake of P by shoot was found to be highest in the treatments that corresponded to FYM 10 t ha^{-1}, biochar 7.5 t ha^{-1}, soil test based POP and soil test based POP + biochar application which were all comparable statistically (Table 94).

With respect to the P uptake by pod, significantly higher value was associated with the application of soil test based POP + biochar (2.150 kg ha^{-1}), followed by the application of biochar 7.5 t ha^{-1} which recorded an uptake of 1.880 kg ha^{-1}, registering a significant difference.

As regards the total uptake the higher value was associated with three treatments *viz.* soil test based POP + biochar, biochar 7.5 t ha^{-1} and FYM 10 t ha^{-1}. As could be anticipated, significantly lowest P uptake by shoot, pod and hence the total uptake was registered in control.

The simple correlation studies had shown that the total P uptake was positively correlated with pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-Mg, $CaCl_2$-S, HCl-Zn and hot water soluble B (Table 92).

Stepwise regression analysis had shown that the variation in total P uptake could be significantly explained to the extent of 77.9 per cent with successive addition of independent variables *viz.* Bray-P and organic carbon (Table 93).

4.5.3.3.5. Potassium content

Potassium content of shoot and pod varied significantly among the treatments (Table 95). The content of K in shoot was higher in the plants which received biochar 10 t ha^{-1} (3.410 %). However, it was comparable with the application of soil test based POP + biochar (3.167 %). With an increase in biochar levels, the K content in shoot increased. Lowest value was associated with the control plots (2.180 %) and it was on par with the application of FYM 10 t ha^{-1} (2.442 %).

Although the content of K in pod was higher for biochar 7.5 t ha^{-1}, it was comparable with the treatments FYM 10 t ha^{-1}, biochar 5 t ha^{-1} and biochar 10 t ha^{-1}. Pods harvested from the control plots recorded lower K content (1.818 %).

The simple correlation studies disclosed that the K content of pod was positively correlated with pH, organic carbon, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg and hot water soluble B (Table 90).

The step wise regression analysis including soil properties that significantly correlated with K content of pod had shown that the variation in this parameter could be significantly attributed to NH_4OAc-Mg status of soil ($R^2 = 0.520^{**}$) (Table 91).

Table 95. Effect of biochar application on potassium content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	2.180	1.818	25.44	9.66	35.10
FYM 10 t ha^{-1}	2.442	2.172	34.35	15.09	49.44
Biochar 5 t ha^{-1}	2.590	2.153	30.90	15.03	45.92
Biochar 7.5 t ha^{-1}	2.927	2.199	42.05	17.38	59.43
Biochar 10 t ha^{-1}	3.410	2.053	40.74	14.19	54.93
Soil test based POP + biochar 10 t ha^{-1}	3.167	2.045	46.37	18.33	64.70
Soil test based POP	2.507	1.917	36.94	14.30	51.24
CD (0.05)	**0.293**	**0.152**	**4.47**	**1.49**	**4.86**

4.5.3.3.6. Potassium uptake

Statistical examination of the data presented in Table 95 showed that there was significant difference between the treatments tried with respect to K uptake, which was found to be higher with the application of soil test based POP + biochar (46.37 kg ha^{-1}). However, it was on par with biochar 7.5 t ha^{-1} (42.05 kg ha^{-1}).

As regards the K uptake by pod, the treatments soil test based POP + biochar and biochar 7.5 t ha^{-1} registered higher values which was on par with each other but superior to rest of the treatments. The residual effect of all other treatments, except control on this parameter was only comparable.

Total K uptake by plants was found to be significantly highest with soil test based POP + biochar application (64.70 kg ha^{-1}). This was followed by the treatment

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biochar 7.5 t ha^{-1} which was on par with biochar 10 t ha^{-1}. Significantly lowest uptake of K by shoot, pod and thus the total was in the control plots.

The simple correlation studies had shown that the total K uptake was positively correlated with pH, organic carbon, CEC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, whereas negatively correlated with HCl-Mn (Table 92).

The stepwise regression analysis yielded equations that could explain 92.1 per cent variability in the total K uptake by plants through CEC, Bray-P and pH (Table 93).

4.5.3.3.7. Calcium content

Data pertaining to the residual effect of various treatments on the concentration of Ca in shoot and pod is presented in Table 96. Concentration of Ca in the shoot was found to be highest in the treatments soil test based POP (2.259 %) and biochar 5 t ha^{-1} (2.193 %). The lowest Ca content was recorded in control (1.907 %) which was on par with soil test based POP (1.957 %).

The content of Ca in pod was found to be higher in the treatments biochar 7.5 t ha^{-1} and biochar 5 t ha^{-1} which were comparable with each other but superior to rest of the treatments. Significantly the lowest value was recorded in control. The residual effect of all other treatments on this parameter was only comparable.

The simple correlation studies had shown that the Ca content of pod was positively correlated with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Cu and hot water soluble boron, whereas negatively correlated with HCl-Mn (Table 90).

The stepwise regression analysis including soil properties that significantly correlated with Ca content of pods had shown that the variation in this parameter could be significantly explained by NH_4OAc-Mg status of soil ($R^2 = 0.698^{**}$) (Table 91).

Table 96. Effect of biochar application on calcium content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	1.907	0.312	22.26	1.657	23.91
FYM 10 t ha^{-1}	2.186	0.355	30.80	2.467	33.26
Biochar 5 t ha^{-1}	2.193	0.447	26.18	3.120	29.30
Biochar 7.5 t ha^{-1}	2.004	0.470	28.82	3.713	32.53
Biochar 10 t ha^{-1}	2.145	0.370	25.66	2.553	28.21
Soil test based POP + biochar 10 t ha^{-1}	1.957	0.393	28.64	3.523	32.16
Soil test based POP	2.259	0.382	33.27	2.853	36.12
CD (0.05)	**0.074**	**0.026**	**2.75**	**0.312**	**2.86**

4.5.3.3.8. Calcium uptake

Uptake of Ca by plants receiving different treatments varied significantly (Table 96). Ca uptake by shoot was higher in the treatment soil test based POP (33.27 kg ha^{-1}), followed by FYM 10 t ha^{-1} (30.80 kg ha^{-1}) which was on par with each other. Regarding the Ca uptake by pod, application of biochar 7.5 t ha^{-1} and soil test based POP + biochar recorded higher values which is superior to all other treatments. This was followed by biochar 5 t ha^{-1} and the difference was significant.

In case of total Ca uptake, the trend was similar to that of the uptake by shoot. As could be anticipated, significantly lowest uptake by shoot, pod and hence the total was registered in control plots.

The simple correlations studies had revealed that the total Ca uptake was positively correlated with organic carbon, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Zn and hot water soluble B (Table 92).

The stepwise regression analysis yielded equations that could explain 66.2 per cent variability in the total Ca uptake through Bray-P and $CaCl_2$-S status of soil (Table 93).

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4.5.3.3.9. Magnesium content

Data on the amount of Mg in the shoot and pod samples as influenced by different treatments is presented in Table 97. The highest Mg content of 0.385 per cent in shoot was noticed in soil test based POP + biochar application, followed by soil test based POP (0.371 %) and the difference was significant. The residual effect of FYM 10 t ha^{-1}, biochar at 5, 7.5 and 10 t ha^{-1} was comparable.

With respect to the Mg content of pods, significantly higher value was observed with the application of FYM 10 t ha^{-1} (0.319 %). This was followed by biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1} application and the difference was significant. The treatments biochar 10 t ha^{-1}, soil test based POP + biochar and soil test based POP application showed a comparable residual effect on this parameter. In both shoot and pod, the control plots registered significantly lower values.

Among the soil properties analysed, Mg content of pod had significant and positive correlation with NH_4OAc-Mg (Table 90).

The stepwise regression analysis including soil properties that correlated with Mg content of pod disclosed that, 21.4 per cent variation in this parameter could be significantly explained by NH_4OAc-Mg (Table 91).

Table 97. Effect of biochar application on magnesium content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	0.264	0.188	3.076	0.998	4.073
FYM 10 t ha^{-1}	0.344	0.319	4.844	2.212	7.056
Biochar 5 t ha^{-1}	0.353	0.277	4.210	1.935	6.146
Biochar 7.5 t ha^{-1}	0.315	0.257	4.538	2.027	6.564
Biochar 10 t ha^{-1}	0.303	0.214	3.623	1.473	5.096
Soil test based POP + biochar 10 t ha^{-1}	0.385	0.210	5.634	1.886	7.519
Soil test based POP	0.371	0.227	5.463	1.695	7.158
CD (0.05)	**0.018**	**0.020**	**0.446**	**0.159**	**0.517**

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4.5.3.3.10. Magnesium uptake

The uptake of Mg by shoot was found to be higher in the treatments *viz.* soil test based POP + biochar and soil test based POP application which was comparable with each other. This was followed by the application of FYM 10 t ha^{-1} and biochar 5 t ha^{-1} and the difference was significant (Table 97).

With respect to the Mg uptake by pod, application of FYM 10 t ha^{-1} recorded the significantly highest value of 2.212 kg ha^{-1}. Residual effect of the treatments biochar 5 t ha^{-1}, biochar 7.5 t ha^{-1} and soil test based POP + biochar on this parameter was comparable.

Regarding the total Mg uptake, the higher value was observed in soil test based POP + biochar application (7.519 kg ha^{-1}) though it was comparable with soil test based POP and FYM 10 t ha^{-1}. Control plots recorded significantly lower Mg uptake.

Total Mg uptake by plants had significant and positive correlation with organic carbon, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, $CaCl_2$-S, HCl-Zn and hot water soluble B (Table 92).

Stepwise regression analysis accounting soil properties that correlated with total Mg uptake revealed that, 66.8 per cent variation in this parameter could be explained by the $KMnO_4$-N status of soil. Further with successive inclusion of independent variables Bray-P, the prediction could be enhanced to 79.7 per cent (Table 93).

4.5.3.3.11. Sulphur content

The concentration of S in shoot did not vary much due to imposed treatments (Table 98). In case of pod, the S content was found to be higher with application of biochar 5 t ha^{-1}, However, it was comparable with all other treatments, except soil test based POP + biochar and soil test based POP which recorded lesser values.

Stepwise regression analysis inclusive of soil properties that correlated with S content (pod) had revealed that, 32.7 per cent variability in S content could be explained by dehydrogenase activity of soil (Table 91).

Table 98. Effect of biochar application on sulphur content and uptake of cowpea

Treatments	Content (%)		Uptake (kg ha^{-1})		
	Shoot	**Pod**	**Shoot**	**Pod**	**Total**
Control	0.034	0.062	0.395	0.331	0.726
FYM 10 t ha^{-1}	0.059	0.066	0.831	0.459	1.290
Biochar 5 t ha^{-1}	0.051	0.077	0.610	0.537	1.146
Biochar 7.5 t ha^{-1}	0.051	0.067	0.743	0.530	1.273
Biochar 10 t ha^{-1}	0.042	0.064	0.502	0.440	0.942
Soil test based POP + biochar 10 t ha^{-1}	0.057	0.045	0.838	0.401	1.239
Soil test based POP	0.055	0.042	0.809	0.314	1.123
CD (0.05)	**NS**	**0.017**	**0.246**	**0.139**	**0.358**

4.5.3.3.12. Sulphur uptake

The uptake of S by shoot was found to be maximum for the treatment soil test based POP + biochar application (0.838 kg ha^{-1}) though it was comparable with all other treatments, except control and biochar 10 t ha^{-1}. In case of pod, the uptake of S was maximum with biochar 5 t ha^{-1} application. However, it was on par with FYM 10 t ha^{-1}, biochar 7.5 t ha^{-1} and 10 t ha^{-1}. The lowest value was recorded in the treatment soil test based POP (Table 98).

Regarding the total S uptake by plants, all the treatments except control showed comparable residual effect. Lowest S uptake was in control plots.

Total S uptake by plants had significant positive correlation with pH, organic carbon, KMnO$_4$-N, NH$_4$OAc-Mg, CaCl$_2$-S, HCl-Zn and hot water soluble B (Table 92).

The stepwise regression analysis between soil properties and total S uptake yielded equations that could explain 58.3 per cent variability in the total S uptake through NH$_4$OAc-Mg and CaCl$_2$-S status (Table 93).

4.5.3.3.13. Iron content

Marked variations had been observed in the Fe content of shoot and pod, due to treatments applied (Table 99). Significantly higher concentration of Fe in both shoot (982.7 mg kg^{-1}) and pod (481.5 mg kg^{-1}) was recorded in the control plots. The treatments biochar 5 t ha^{-1} and 7.5 t ha^{-1} had registered significantly lowest concentration of Fe in shoot. In case of Fe content in pod, the lowest value was associated with the treatments soil test based POP (235.4 mg kg^{-1}) and soil test based POP + biochar application (250.5 mg kg^{-1}). With an increase in biochar application rate, the concentration of Fe in cowpea pod decreased and the decrease was also significant.

The simple correlation studies had indicated that the Fe content of pod was significantly and negatively related to pH, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, HCl-Zn, HCl-Cu and hot water soluble B, whereas positively to HCl-Mn content of soil (Table 90).

Attempts to quantify the contribution of soil properties on concentration of Fe in pod through stepwise regression had revealed that, 61.7 per cent of the variation in this parameter could be significantly explained by MBC status of soil. With further inclusion of CEC and Bray-P, 90.2 per cent variability could be explained (Table 91).

Table 99. Effect of biochar application on iron content and uptake of cowpea

Treatments	**Content (mg kg^{-1})**		**Uptake (kg ha^{-1})**		
	Shoot	**Pod**	**Shoot**	**Pod**	**Total**
Control	982.7	481.5	1.144	0.255	1.400
FYM 10 t ha^{-1}	743.4	343.3	1.047	0.238	1.285
Biochar 5 t ha^{-1}	597.8	326.2	0.714	0.228	0.942
Biochar 7.5 t ha^{-1}	577.4	300.3	0.830	0.237	1.067
Biochar 10 t ha^{-1}	725.8	267.6	0.867	0.185	1.052
Soil test based POP + biochar 10 t ha^{-1}	732.6	250.5	1.071	0.225	1.296
Soil test based POP	751.8	235.4	1.107	0.176	1.283
CD (0.05)	**40.8**	**18.8**	**0.064**	**0.025**	**0.083**

4.5.3.3.14. Iron uptake

Uptake of Fe by shoot was found to be significantly influenced by the treatments imposed, wherein the control plots (1.144 kg ha^{-1}) and soil test based POP

(1.107 kg ha^{-1}) had registered higher values which were comparable. Significantly lower value was recorded by application of biochar 5 t ha^{-1} (0.714 kg ha^{-1}) (Table 99).

As regards the uptake of Fe by pod, the higher value of 0.255 kg ha^{-1} was noticed in the control. However, it was comparable with FYM 10 t ha^{-1} and biochar 7.5 t ha^{-1} application. The lowest value was registered by two treatments *viz*. biochar 10 t ha^{-1} and soil test based POP application. Total Fe uptake by plants was significantly higher in the control (1.400 kg ha^{-1}) and was lower in biochar 5 t ha^{-1} (0.942 hg ha^{-1}).

The simple correlation studies unwinded the negative and significant relationship of total Fe uptake with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca and NH_4OAc-Mg and hot water soluble B. It was further noticed that the correlation between HCl-Mn and total Fe uptake was negative (Table 92).

The stepwise regression analysis including soil properties that correlated with the total Fe uptake had shown that, 56.5 per cent variation in this parameter could be significantly explained by NH_4OAc-Ca status of soil (Table 93).

4.5.3.3.15. Manganese content

Concentration of Mn in both shoot and pod was found to be significantly highest in the control plots. Lower Mn content in shoot was recorded by biochar 10 t ha^{-1} application, whereas in pods, application of biochar 10 t ha^{-1} and soil test based POP + biochar recorded lower concentrations. With an increase in biochar application rate, the concentration of Mn in both shoot and pod decreased significantly (Table 100).

Simple correlation studies had revealed that the Mn content of pods was positively correlated with HCl-Fe, whereas negatively with pH, organic carbon, CEC, dehydrogenase activity, Bray-P, NH_4OAc-K, NH_4OAc-Ca, HCl-Zn, HCl-Cu and hot water soluble B (Table 90).

Stepwise regression analysis considering soil properties that correlated with Mn content (pod) had further shown that, the concentration of Mn can be significantly altered by HCl-Zn and HCl-Cu, to the extent of 83 per cent (Table 91).

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Table 100. Effect of biochar application on manganese content and uptake of cowpea

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	702.0	122.83	0.818	0.065	0.884
FYM 10 t ha^{-1}	650.8	96.43	0.917	0.067	0.984
Biochar 5 t ha^{-1}	480.3	112.20	0.573	0.079	0.652
Biochar 7.5 t ha^{-1}	426.4	77.60	0.612	0.061	0.673
Biochar 10 t ha^{-1}	368.0	61.27	0.441	0.042	0.483
Soil test based POP + biochar 10 t ha^{-1}	412.0	62.77	0.604	0.056	0.660
Soil test based POP	519.9	78.77	0.765	0.059	0.824
CD (0.05)	**40.7**	**9.61**	**0.074**	**0.016**	**0.075**

4.5.3.3.16. Manganese uptake

The uptake of Mn by shoot was found to be significantly higher in the treatment FYM 10 t ha^{-1} (0.917 kg ha^{-1}) (Table 100). This was followed by control (0.818 kg ha^{-1}) and soil test based POP application (0.765 kg ha^{-1}) which were on par with each other. The treatment biochar 10 t ha^{-1} recorded significantly lowest value (0.441 kg ha^{-1}).

With regard to the Mn uptake by pod, maximum uptake was associated with the treatments biochar 5 t ha^{-1}, FYM 10 t ha^{-1} and control. The uptake was minimum with application of biochar at 10 t ha^{-1}.

Regarding the total Mn uptake, application of FYM 10 t ha^{-1} had registered significantly highest value. This was followed by control and soil test based POP which showed equal performance. Significantly lowest value was recorded in biochar 10 t ha^{-1}. The total Mn uptake decreased with an increase in the biochar application rate similar to that of its concentration in pod.

Among the soil properties, the total Mn uptake had a significant negative correlation with pH, organic carbon, CEC, NH_4OAc-K, NH_4OAc-Ca, HCl-Cu and hot water soluble B, whereas positive correlation with HCl-Mn (Table 92).

The stepwise regression analysis accounting soil properties that correlated with total Mn uptake had shown that the variation in this parameter could be significantly controlled by HCl-Mn and NH_4OAc-K content of soil to the extent of 83.5 per cent (Table 93).

4.5.3.3.17. Zinc content

The concentration of Zn in shoot was found to be statistically higher in control, whereas the same treatment recorded significantly lowest Zn in pods (Table 101). Similarly, the treatment biochar 10 t ha^{-1} which recorded lowest Zn content in shoot (35.30 mg kg^{-1}) produced pods with higher Zn content (66.93 mg kg^{-1}). However, it was on par with the treatments biochar 5 t ha^{-1}, biochar 7.5 t ha^{-1} and soil test based POP + biochar application. With an increase in the levels of biochar, concentration of Zn in pods increased, however there were no marked difference within them.

The simple correlation studies had revealed that the Zn content of pods was positively correlated with pH, organic carbon, CEC, MBC, dehydrogenase activity, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, and negatively with HCl-Mn (Table 90).

The stepwise regression analysis including all soil properties that correlated with Zn content (pod) had revealed that, 81.4 per cent variation in this parameter could be significantly explained by CEC and organic carbon content of soil (Table 91).

4.5.3.3.18. Zinc uptake

The uptake of Zn by shoot was found to be maximum in the control plots, whilst the same treatment resulted in lowest Zn uptake in case of pod (Table 101). Highest Zn uptake by pod was recorded with the application of soil test based POP + biochar (0.060 kg ha^{-1}).

With respect to the total Zn uptake, significantly higher uptake was recorded in plots which received soil test based POP + biochar (0.121 kg ha^{-1}), followed by biochar 7.5 t ha^{-1} (0.110 kg ha^{-1}) and the difference was significant. The residual effect of all other treatments on this parameter was comparable.

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From the simple correlation studies, it was seen that the total Zn uptake had a positive relationship with CEC, dehydrogenase activity, $KMnO_4$-N, Bray-P and hot water soluble B (Table 92).

The stepwise regression analysis including soil properties that correlated with total Zn uptake revealed that, 39.4 per cent variation in this parameter could be explained by the dehydrogenase activity of soil (Table 93).

Table 101. Effect of biochar application on zinc content and uptake of cowpea

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Shoot	**Pod**	**Shoot**	**Pod**	**Total**
Control	61.93	44.03	0.072	0.024	0.096
FYM 10 t ha^{-1}	37.60	54.63	0.053	0.038	0.091
Biochar 5 t ha^{-1}	41.10	64.63	0.049	0.045	0.094
Biochar 7.5 t ha^{-1}	40.60	64.87	0.058	0.051	0.110
Biochar 10 t ha^{-1}	35.30	66.93	0.042	0.046	0.088
Soil test based POP + biochar 10 t ha^{-1}	41.87	66.43	0.061	0.060	0.121
Soil test based POP	37.93	57.60	0.056	0.043	0.099
CD (0.05)	**3.77**	**5.33**	**0.009**	**0.005**	**0.010**

4.5.3.3.19. Copper content

It can be seen from the Table 102 that the concentration of Cu in shoot was higher in soil test based POP application (14.53 mg kg^{-1}) which was comparable with FYM 10 t ha^{-1} (14.03 mg kg^{-1}). The lowest content of Cu in shoot was observed in control plots. With an increase in biochar application rate, the concentration of Cu in shoot increased, however the increase was only marginal.

As regards the Cu content in pod, the treatment biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1} registered higher values which were on par with each other. Unlike the shoot, the concentration of Cu in pod decreased with an increase in biochar application rate, lowest value showing association with control.

Table 102. Effect of biochar application on copper content and uptake of cowpea

Treatments	Content (mg kg^{-1})		Uptake (kg ha^{-1})		
	Shoot	Pod	Shoot	Pod	Total
Control	10.73	11.77	0.013	0.007	0.019
FYM 10 t ha^{-1}	14.03	16.33	0.019	0.011	0.031
Biochar 5 t ha^{-1}	11.93	20.13	0.014	0.014	0.028
Biochar 7.5 t ha^{-1}	12.53	19.53	0.018	0.015	0.033
Biochar 10 t ha^{-1}	13.03	13.47	0.016	0.009	0.025
Soil test based POP + biochar 10 t ha^{-1}	12.20	12.43	0.018	0.011	0.029
Soil test based POP	14.53	14.93	0.021	0.011	0.033
CD (0.05)	**1.37**	**1.84**	**0.002**	**0.002**	**0.007**

The simple correlation studies made out the positive and significant relationship of copper content (pod) with NH_4OAc-Ca and NH_4OAc-Mg status of soil (Table 90). Furthermore, the stepwise regression analysis including soil properties that correlated with Cu content (pod) had revealed that, 58.1 per cent variation in this parameter could be explained by NH_4OAc-Ca and NH_4OAc-Mg (Table 91).

4.5.3.3.20. Copper uptake

The uptake of Cu by plants as influenced by different treatments is presented in the Table 102. The residual effect of different treatments on the Cu uptake by shoot was similar to that of its concentration in shoot. As regards the pod, the higher uptake was associated with the application of biochar 5 t ha^{-1} and 7.5 t ha^{-1} which was superior to rest of the treatments and the lowest was in control. Regarding the total Cu uptake, the residual effect of different treatments was comparable, though the higher value was observed in biochar 7.5 t ha^{-1} and soil test based POP application. The lowest uptake was in control.

The simple correlation analysis had shown that the total Cu uptake was positively related with pH, organic carbon, CEC, MBC, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, whereas it was negative with HCl-Mn (Table 92).

The stepwise regression analysis including soil properties that correlated with total Cu uptake had further revealed that, 43.1 per cent variability in this parameter could be explained by Bray-P alone and with further inclusion of NH_4OAc-Mg and $KMnO_4$-N, 69.4 per cent variability could be explained (Table 93).

4.5.3.3.21. Boron content

Concentration of B in shoot was found to be highest in the treatments which included biochar 10 t ha^{-1} and biochar 5 t ha^{-1} and the lowest was in control. The differences were significant as well (Table 103). All other treatments had comparable residual effect on this parameter. With respect to the higher concentration of B in pods, the effect was shared by three treatments *viz*. FYM 10 t ha^{-1}, biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1}. Numerically lowest value was observed in control.

Boron content of pod had a positive correlation with pH and NH_4OAc-Mg, whereas the correlation was negative with HCl-Fe (Table 90). Furthermore, the stepwise regression analysis between soil properties that correlated with B content (pod) had shown that, 61.0 per cent variation in this parameter could be accounted to NH_4OAc-Ca and HCl-Fe (Table 91).

Table 103. Effect of biochar application on boron content and uptake of cowpea

Treatments	**Content (mg kg^{-1})**		**Uptake (kg ha^{-1})**		
	Shoot	**Pod**	**Shoot**	**Pod**	**Total**
Control	56.77	22.77	0.066	0.012	0.078
FYM 10 t ha^{-1}	64.60	43.10	0.091	0.030	0.121
Biochar 5 t ha^{-1}	78.93	40.03	0.094	0.028	0.122
Biochar 7.5 t ha^{-1}	68.93	39.50	0.099	0.031	0.13
Biochar 10 t ha^{-1}	79.93	32.67	0.096	0.023	0.118
Soil test based POP + biochar 10 t ha^{-1}	69.10	22.87	0.101	0.020	0.121
Soil test based POP	66.37	24.27	0.098	0.018	0.116
CD (0.05)	**6.39**	**3.71**	**0.01**	**0.004**	**0.017**

4.5.3.3.22. Boron uptake

Though there were differences in the B uptake by shoot between the treatments, it was only marginal. However, a numerically higher value was recorded by soil test based POP + biochar application (0.101 kg ha^{-1}) and significantly lowest uptake was observed in control (Table 103). Regarding the B uptake by pod, the higher values were associated with the application of FYM 10 t ha^{-1}, biochar 5 t ha^{-1} and biochar 7.5 t ha^{-1} which were on par with each other but superior to all other treatments. The lowest uptake was in control. With respect to the total B uptake, the trend was similar to that of the shoot uptake.

The simple correlation studies showed that the total B uptake was positively related with pH, organic carbon, CEC, MBC, $KMnO_4$-N, Bray-P, NH_4OAc-K, NH_4OAc-Ca, NH_4OAc-Mg, HCl-Zn, HCl-Cu and hot water soluble B, and negatively with HCl-Mn (Table 92).

It was further indicated by the stepwise regression analysis that 73.2 per cent variability in the total B uptake could be explained by organic carbon content of soil and with inclusion of NH_4OAc-Mg, variability could be explained to 81.5 per cent (Table 93).

Discussion

5. DISCUSSION

This chapter deals with interpretations on results obtained from the study titled "Aggrading lateritic soils (Ultisol) using biochar" carried out at Department of Soil Science and Agricultural Chemistry, College of Horticulture, Vellanikkara and Agricultural Research Station, Mannuthy, during the period 2016-2018. This chapter is arranged under different subheadings namely

- Characterization of the biochar
- Characterization of the experimental soil
- Dynamics of carbon and nitrogen in soil
- Direct and residual effect of biochar on post-harvest soil properties
- Direct and residual effect of biochar on growth attributes and yield
- Direct and residual effect of biochar on quality parameters
- Direct and residual effect of biochar on nutrient content and uptake by crop

5.1. Characterization of the biochar

The role of biochar in sequestering carbon and improving soil fertility is a proven fact but the material effect is dependent on the initial raw material and pyrolysis temperature, to arrive at which, it has to be characterized in terms of physical and chemical properties.

5.1.1. Physical, electro-chemical and chemical properties

The recovery of biochar in this study, from the specially fabricated kiln was 22 per cent. Reports say that the recovery of final finished product is dependent on mean resident time and pyrolysis temperature. Another influencing factor is the type of biological material used for biochar production. Elangovan (2014) reported recovery percentage of 12 to 40, when pyrolysis was done using different biological residues.

Bulk density and particle density of the produced biochar was 0.128 and 0.833 Mg m^{-3}, respectively. This lower values when compared to the soil indicated its promising role in reducing the soil bulk density and increasing the porosity thereby its capability to hold more water when applied to soil. This statement holds good in the present work where the biochar recorded the WHC of 307.7 per cent. Another reason for the increased water holding capacity of biochar is the high surface area of its particles. Similar observations on physical properties of biochar has also been reported by Saranya *et al.* (2011), Ippolito *et al.* (2012), Shenbagavalli and Mahimairaja (2012), Dainy (2015), Angalaeeswari and Kamaludeen (2017) and Rajalekshmi (2018).

The porosity value of 84.63 per cent obtained for biochar in the present study is due to the desiccation of biological tissue and emission of structural H_2O, CO_2, CO and H_2 from it during pyrolysis, as suggested by Downie *et al.* (2009). In fact, the process of pyrolysis creates more of internal porosity within biochar particles.

The pH of coconut based biochar was alkaline touching a value of 10.01 which may be the effect of sufficient quantity of ash resulting from the pyrolysis of biological materials (11.33 % ash in this case). In addition, dominance of carbonates of alkali and alkaline earth metals in biochar in general also would have contributed to the alkaline pH registered. Hydrolysis of salts of Ca, Mg and K would make the biochar alkaline as reported by Gaskin *et al.* (2008) and Singh *et al.* (2010). Baernthalera (2006) reported a higher concentration of bases in biochars produced from grasses and crop residues as against that from softwood and hardwood.

The varying amounts of silica, sesquioxides, phosphates, heavy metals, high concentration of carbonates of alkali and alkaline earth metals and small quantities of organic and inorganic nitrogen recorded in the biochar explains its high electrical conductivity (3.42 dS m^{-1}), which was further reaffirmed through FT-IR spectroscopy (Fig. 2).

The CEC of biochar obtained in the present study was 15.78 cmol (+) kg^{-1} and the relatively high value of CEC noticed is ascribed to the formation of graphene sheet with a polyaromatic structure during the process of pyrolysis which give rise to large amounts of reactive surfaces wherein a wide range of organic molecules both polar and non-polar and inorganic ions can get sorbed. Production temperature above 350°C lead to prominence of aromatic carbon groups and a range of varying functional groups on the surface of graphene sheets. Furthermore, H, N, O, P and S gets incorporated in the aromatic rings making it more electron negative thus increasing CEC. Increase in charge density per unit surface of organic matter, which equates with a greater degree of oxidation or increase in surface area for cation adsorption, or a combination of both would also have resulted in higher CEC. Works conducted with biochar have revealed that its CEC ranged between 12.5 and 38.63 cmol (+) kg^{-1} (Elangovan, 2014; Akshatha, 2015; Dainy, 2015; Kamara *et al.*, 2015; Yang *et al.*, 2015).

The values on carbon content of biochar (64.14 %) obtained from the present study revealed its highly carbonaceous nature (Fig. 4). Essentially, biochar is amorphous but chances are that it may contain crystalline structure locally of highly ordered graphene sheets (Downie *et al.*, 2009), which was further confirmed through TEM (Plate 20a-20f). The high carbon storage associated with biochar can be directly related with the high C content in the raw material (Lee *et al.*, 2013). The stability of biochar in the environment is contributed by the condensed aromatic nature comprising of conjugated aromatic compounds of six carbon atoms linked together in rings. The C: N ratio of biochar was 113:1 and it was comparable with results obtained for evaluating the chars produced from different bio-wastes by Cheng *et al.* (2006), Rondon *et al.* (2007), Novak *et al.* (2009), Ameloot *et al.* (2013), Wiedner *et al.* (2013), Shenbagavalli and Mahimairaja (2012), Elangovan (2014) and Dainy (2015).

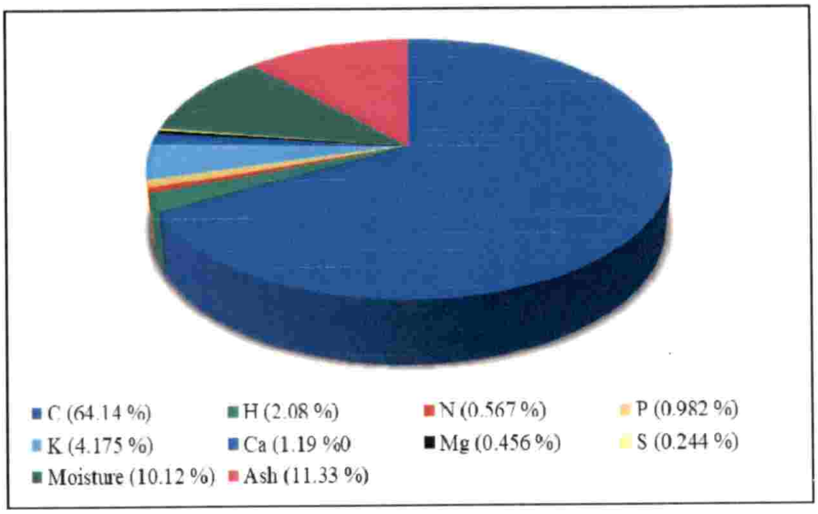

Fig. 4. Composition of biochar

The process of pyrolysis or oxidation that generates biochar causes some of the nutrient especially at the surface to volatilize because of the continuous heating and some other nutrient to get concentrated in the remaining biochar. Of all the macronutrients, N is the most sensitive which means the N contained in a high temperature will always be on the lower side as reported by Tryon (1948). In the present investigation also N content was recorded as 0.567 per cent only as against 0.982, 4.175 and 1.19 per cent in case of P, K and Ca. The content of Mg and S was 0.456 and 0.244 per cent, respectively. Further it also contained micronutrients *viz.* iron (1535 mg kg^{-1}), manganese (83.95 mg kg^{-1}), zinc (53.93 mg kg^{-1}), copper (35.5 mg kg^{-1}) and boron (55.0 mg kg^{-1}) in appreciable amounts.

On heating a plant tissue, the organic C starts to volatilize at about 100°C, whereas P will not until the temperature is around 700°C (Knoepp *et al.*, 2005). Usually the availability of P from plant tissue is improved a lot when the organic material is subjected to combustion / charring. This is made possible by disproportionately volatilizing carbon and by cleaving organic P bonds leading to accumulation of P salts in the charred material. The higher levels of K, Ca and Mg is associated with hydrolysis of alkaline earth metals during the heating process.

The main intention of biochar application is as a carbon sequestrant and not as a nutrient source. The principle behind testing the basicity and/or acidity of a material is to find out its suitability in regulating pH of the system/ environment. The biochar produced in the present study was subjected to base or acid uptake and the values were 2.02 and 0.08 mmol g^{-1}, respectively. The higher basicity adds on to the alkaline nature of the material already discussed.

5.1.2. Surface morphology of biochar

While the physical, electro-chemical and chemical characterization of biochar gives idea on the physical makeup and chemical composition of biochar, it is the microscopic image that reveals surface morphology. In the present study SEM and TEM images were taken for in depth study of the external and internal morphology of the biochar, respectively.

The SEM and TEM micrographs of biochar developed at different spatial resolutions and magnifications were depicted under results in Plate 19 and 20, respectively. The SEM image exhibited highly disordered and complex morphology with longitudinal channels and pores, which disclosed the porous nature of biochar which was quantitatively assessed as 84.63 per cent. In common biochar retains the cell wall structure of the feedstock which was further endorsed in SEM image. Pores which were generated by the pyrolysis process were visible in different shapes and size and remained scattered over the surface. Low lignin and high volatile matter content of feedstock were identified as the properties that affects the formation of pores in biochar by Lehmann *et al.* (2011). The feedstock used in the present study was coconut husk and shell with high fibre content, which in turn added to the porous biochar as evidenced through the SEM image.

The internal properties of biochar studied using the TEM showed the presence of localized crystalline graphite like structure in it, which further conveys that carbon is the most dominant element of the experimental biochar. The results are in accordance with the findings of Downie *et al.* (2009), Hu *et al.* (2010), Luo *et al.* (2011), Shenbagavalli and Mahimairaja (2012), Manikandan and Subramanian (2013), Shalini (2013), Elangovan (2014) and Gokila and Baskar (2015).

5.1.3. Structural chemistry of biochar

Majority of the chemical interactions between biochar and soil environment are directly related to the structural chemistry of biochar and hence the facilities on FT-IR and Raman spectroscopy were made use of in the present project for studying the structural chemistry of the biochar generated. The FT-IR and Raman spectrum of biochar thus obtained are depicted in Fig. 2 and 3, respectively. There were totally 13 and 25 strong absorption peaks for FT-IR and Raman spectrum. Each peak was assigned with a corresponding functional group (4.1.2.1. and 4.1.2.2). The representative peaks for aromatic carbon appeared more clearly, such as C=C stretching (1583.97, 1472, 1500, 1590 cm^{-1}), C-O stretching (1112.23, 1642 cm^{-1}) and C-C stretching (756.05 cm^{-1}). Both the FT-IR and Raman spectrum clearly showed the absence of aliphatic groups and presence of more number of aromatic carbon groups, which indicates the recalcitrant nature of biochar carbon. In general, the recalcitrant nature of biochar gets increased with increase in number of aromatic groups. In addition to this, both the methods clearly explained that the produced biochar contained higher amount of C, H, O and traces of N, S, P and Si on its surface.

On the whole, the presence of functional groups like carboxyl and hydroxyl, as visualized through the FT-IR and Raman spectrum suggested that the biochar produced from coconut husk and shell in this study can be used as a soil amendment for improving the properties of lateritic soils, especially with reference to pH, CEC besides serving as a potential adsorbent. This closely matches with the findings of Yuan *et al*. (2011), Jindo *et al*. (2014) and Mary *et al*. (2016).

5.2. Characterization of the experimental soil

On characterizing, the experimental soil was found to be sandy clay loam in texture with 32.5 per cent of finer fraction *viz.* clay and silt and 63.7 per cent of sand fraction, indicating its freedom from textural constraints. Taxonomically it is classified as Typic plinthustults. The bulk density of soil was 1.23 Mg m^{-3} and the pore space was 47.64 per cent pointing out the free draining nature. With respect to the pH and EC, the soil was strongly acidic and non-saline. The organic carbon content was 1.55 per cent and the cation exchange capacity 3.72 cmol (+) kg^{-1}, which showed the dominance of kaolinite.

With respect to the available nutrient status, it was found to be low in $KMnO_4$-N, medium in Bray-P and high in NH_4OAc-K. Among the secondary nutrients, Ca and S was found to be in sufficient range, whereas the element Mg was deficient in the experimental soil. All the micronutrients tested, except boron were in the sufficient range.

5.3. Incubation experiment

The carbon and nitrogen dynamics in the experimental soil were studied by conducting an incubation experiment for a time span of 15 months within which samples were drawn at intervals of 0, 3, 6, 9, 12 and 15 months after incubation. Total C, organic C, water soluble C (WSC), hot water soluble C (HWSC), permanganate oxidizable C (POXC) and microbial biomass C (MBC) constituted the various fractions of carbon analysed, whereas the nitrogen fractions consisted of both inorganic (NH_4-N and NO_3-N) and organic [Total hydrolysable (THyN), Amino acid N (AAN)]. In addition, $KMnO_4$-N and total N were also quantified.

5.3.1. Dynamics of carbon

Carbon is essential to all life on earth being the principle component of living organisms. Soil constitutes the largest dynamic reservoir of carbon on earth which makes it a critical component of the global carbon cycle. In soil, the carbon is mostly bound with soil organic matter consisting of the dead biomass from roots, plant litter, animals and microorganisms along with the live organisms which actively consume and produce a diverse mixture of carbon containing compounds. It is the biogeochemical cycle of carbon in the earth system that controls the fluxes, pools and transformations associated with this life's most fundamental element. In order to characterize the amount of carbon stored in the given reservoir, be it atmosphere, terrestrial or aquatic, the time needed to exchange each carbon atom of the system otherwise called as mean residence time and also the physical or chemical state of carbon in a given reservoir or as it exchanges among the reservoirs are essential to be characterized. Based on the mean residence time a particular system can be further divided into active/labile pool (1-5 years MRT), slow pool (20-40 years MRT) and passive/inactive/recalcitrant pool (200-1500 years MRT). In general, the labile carbon pool has a greater turnover rate (shorter MRT in soil) of several weeks/months/years as against the recalcitrant pools (Paul *et al.*, 2001) and thus, the labile pools like MBC, WSC, HWSC, POXC have been suggested as early indicators of the effects of land use changes on soil organic matter quality (Gregorich *et al.*, 1994; Bolinder *et al.*, 1999, Ghani *et al.*, 2003; Banger *et al.*, 2010).

5.3.1.1. Water soluble carbon

WSC, the product of SOM decomposition which is sorbed on soil or sediment particles or dissolved in soil water serve as a main energy source for the soil biota in addition to providing nutrients like N, P and S in the mineralizable form and influencing availability of metal ions in soil by forming soluble complexes (Stevenson, 1994). WSC content ranged from 92.61 to 111.5 mg kg^{-1} with the treatment FYM 10 t ha^{-1} recording the highest. Over the period of incubation, it showed an increase only upto the first 6 months which was significant, whereas, the reduction noticed in the last two phases of incubation (12 and 15 months) was only marginal (Fig. 5). The rate of decomposition of the material decides the amount of WSC in the system. On comparing the efficacy of FYM which registered the highest value of 111.5 mg kg^{-1} with biochar, the statement gets substantiated further. The initial increase noticed for upto 6 months of incubation may be due to the increased rate of decomposition of added organic sources and the reduction towards the fag end of incubation is directly ascribed to the reduction in the mineralization rate and also the increased consumption of WSC as an energy source by the microorganisms involved. The positive correlation observed between WSC and POXC, MBC further supports the more intense activity of microorganisms and thus more decomposition of SOM and labile organic carbon. Such a positive correlation of WSC with MBC has also been reported by Demise *et al.* (2014) and Sparling *et al.* (1998). The result also confirmed by the highest dehydrogenase activity recorded in biochar treatment in the present study.

5.3.1.2. Hot water soluble carbon

HWSC is a sensitive indicator of the ecosystem changes. Being a component of the labile SOM and also being closely related to soil microbial biomass and micro aggregation it can be used as one of the soil quality indicators in soil plant continuum. This fraction extracted after WSC, using hot distilled water extracts soil microbial biomass, simple organic compounds and compounds which are hydrolysable under the given extraction conditions (Weigel *et al.*, 2011). Plenty of literature designates its extraction as near to nature conditions of the ongoing mineralization process. Here also the treatment FYM 10 t ha^{-1} registered the highest value for HWSC as in the case of WSC. However, the treatments and days of incubation had a strong effect on its content as evidenced by a decline noticed over the incubation period (Fig. 6). Considering the trends in changes in content of WSC and HWSC on incubation, it can be said that the HWSC which constitutes the soil microbial biomass, simple organic compounds and easily hydrolysable carbon might have decomposed and converted into WSC. This may be reason for decline in the HWSC carbon over incubation and the corresponding increase in the WSC (Demise *et al.*, 2014).

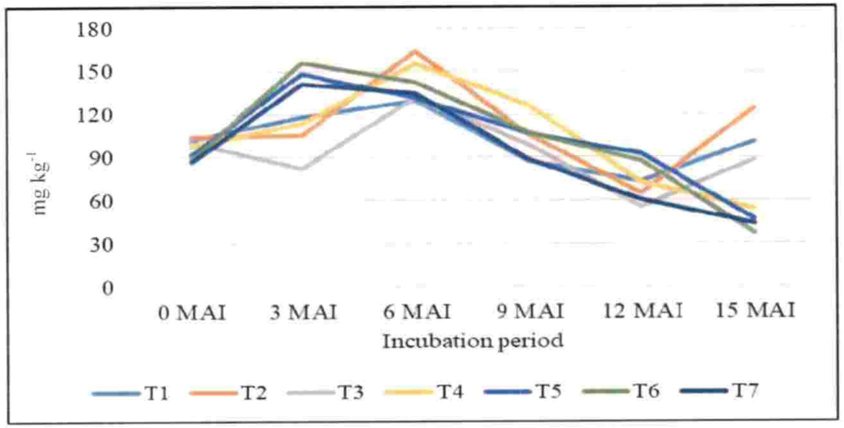

Fig. 5. Changes in the water soluble carbon content (mg kg^{-1}) at different stages of incubation

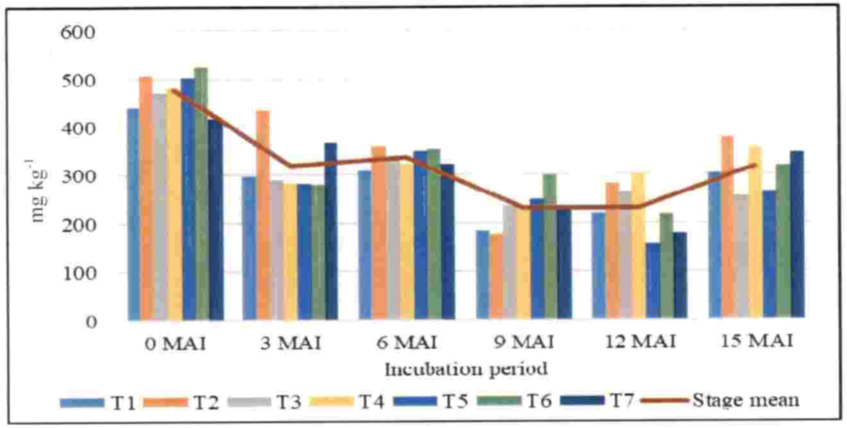

Fig. 6. Changes in the hot water soluble carbon content (mg kg^{-1}) at different stages of incubation

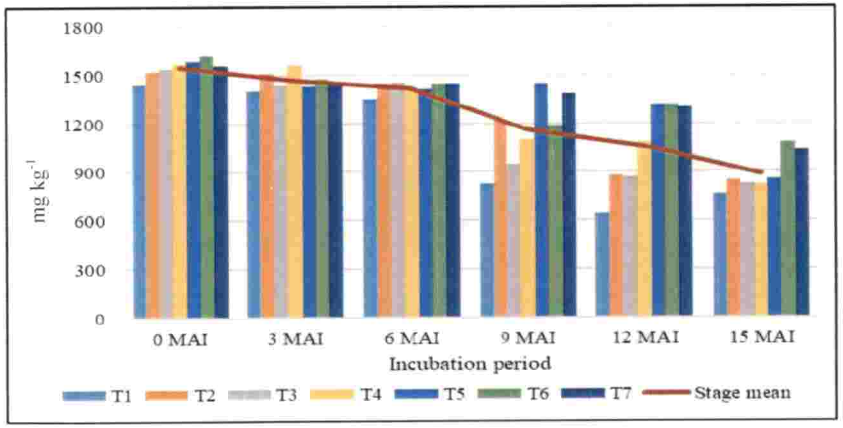

Fig. 7. Changes in the POXC content (mg kg^{-1}) at different stages of incubation

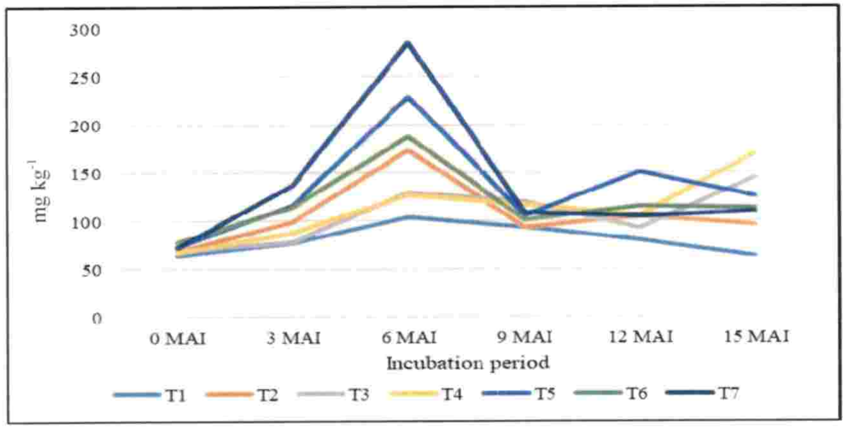

Fig. 8. Changes in the MBC content (mg kg^{-1}) at different stages of incubation

Hot water soluble carbon had positive relationship with organic carbon, total carbon, NH_4-N and total N, which showed its influence on the process of mineralization and capacity as a tool for determining the easily available pool of mineralizable N.

5.3.1.3. Permanganate oxidizable carbon

The next in the series of labile carbon fractionated was the POXC, which encompasses all readily oxidizable organic components including humic materials and polysaccharides, which generally accounts for 5 – 30 per cent of SOC (Blair *et al*., 1995; Blair, 2000; Gragham *et al*., 2002). This is usually extracted using a weak potassium permanganate solution (333 *mM*). Culman *et al*. (2012) stated that the POXC was closely related with the smaller and heavier particulate organic carbon, indicating that POXC reflects a relatively stabilized pool of active soil carbon.

From the results given in Table 15, it could be inferred that the POXC content showed a signicant decrease with advancement of incubation, where it reduced to 890.2 mg kg^{-1} from 1549.8 mg kg^{-1} recorded at the start of incubation, irrespective of treatments. The POXC content registered was comparable in respect of soil test based POP, soil test based POP + biochar and biochar 10 t ha^{-1}. The soil alone treatment *i.e.* the control registered the lowest value for POXC (Fig. 7). An increase in biochar level brought about increase in the content of POXC also. Unlike WSC and HWSC, a continuous reduction was noticed in the content of POXC during incubation. The decrease was significant at every stage of incubation in the case of biochar 10 t ha^{-1}, soil test based POP + biochar and soil test based POP treatments. At all the stages of incubation the POXC content was lower in the control.

In order to ascertain the effect of incubation over POXC content, simple regression analysis was done which revealed that in all the treatments the days of incubation had a significant effect on the content of POXC. On comparing the treatments, the soil alone treatment recorded the maximum rate of decrease, whereas, the minimum rate of decrease of 0.993 mg kg^{-1} day^{-1} was associated with soil test based POP treatment. Including NPK fertilizer along with biochar added on to the rate of reduction in POXC. The addition of carbon rich material together with easily available inorganic N source would have helped in proliferation of soil

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microorganisms resulting in faster depletion of labile carbon pool (POXC). This is in agreement with the findings of Manna *et al.* (2007).

The result was further confirmed by obtaining a significant and positive correlation with all the carbon fractions studied namely WSC, HWSC, organic carbon and total carbon and also with nitrogen fractions like NH_4-N, THyN and total N. however, its relationship with NO_3-N, AAN and $KMnO_4$-N proved negative.

5.3.1.4. Microbial biomass carbon

In any soil, microbial biomass is a key component because it defines the functional component of the soil biota which are primarily responsible for decomposition, SOM turnover and nutrient transformations (Smith and Paul, 1990; Witter, 1996). According to Gil-Sotres *et al.* (2005), microbial biomass carbon can be used as an approach to evaluate soil quality. Microbial biomass also is a transformation matrix for all natural organic materials in the soil and act as a labile reservoir of plant available nutrients (Jenkinson and Ladd, 1981). MBC is a measure of carbon contained within the living component of SOM, consists of bacteria and fungi and makes up about 1-5 per cent of total SOC.

From the results it could be inferred that MBC was lowest in soil alone treatment, whereas it was highest in soil applied with soil test based POP and biochar at 10 t ha^{-1}. Another noticeable feature was the increase in MBC content with increase in the biochar levels (Fig. 8). The porous nature of biochar, its high surface area, ability to adsorb soluble organic matter and inorganic nutrients would have provided a suitable niche for the microbes which is in conformity with the findings of Thies and Rillig (2009) and Shenbagavalli and Mahimairaja (2012). The improvement in soil physical and chemical environment thus providing a favourable habitat has also been pointed out by Lehmann *et al.* (2011) and Jien and Wang (2013) as the favourable after effect of biochar application.

On analysing the effect of incubation period on MBC, it was seen that the content got increased and reached a maximum at 6 months and declined thereafter. Treatment effect was significant only upto 9 months of incubation. In addition, a significant difference was also noticed on considering the interaction of incubation period with treatments. MBC was the lowest in the control at all stages of incubation and also in all the treatments except control, the lowest MBC was registered during the 0th month of incubation.

The increasing trend in MBC content noticed during the first six months and its decline thereafter is attributable to the content of WSC which also showed the similar trend for the first six months of incubation. This can further be explained from the fact that it is the WSC that serve as the immediate source of energy for soil microorganisms, a reduction in which will reflect negatively on the microbial activity. The positive and significant correlation obtained between the MBC and WSC matches well with the explanation.

5.3.1.5. Total carbon

An information on total carbon which is the summation of three carbon forms namely organic, elemental (which is insignificant in most soils) and inorganic (usually carbonates and bicarbonates) is essential for understanding the different components of SOM. Generally, in lateritic soils, the content of total carbon almost equates with the organic carbon.

A perusal of total carbon value in the incubation experiment showed that the content decreased initially, followed by an increase upto six months of incubation after which it decreased further. Considering the treatment effect it was seen that the soil test based POP + biochar registered a significantly higher value followed by biochar application at the highest rate. Control recorded the lowest value for the total carbon (1.983 %) (Fig. 9). Increasing the quantity of biochar made an increase in total carbon level also which was also statistically significant. The interaction of incubation period with treatments made a significant effect on total carbon content. However, soil alone treatment registered the lowest value at all the stages of incubation. Throughout the incubation period the highest value of total carbon was associated with the treatment biochar 10 t ha^{-1} and soil test based POP + biochar, which were comparable statistically as well. The highly carbonaceous nature of biochar (64.14 %) is directly responsible for the improvement in total carbon, on incubation. Ample research findings support this observation.

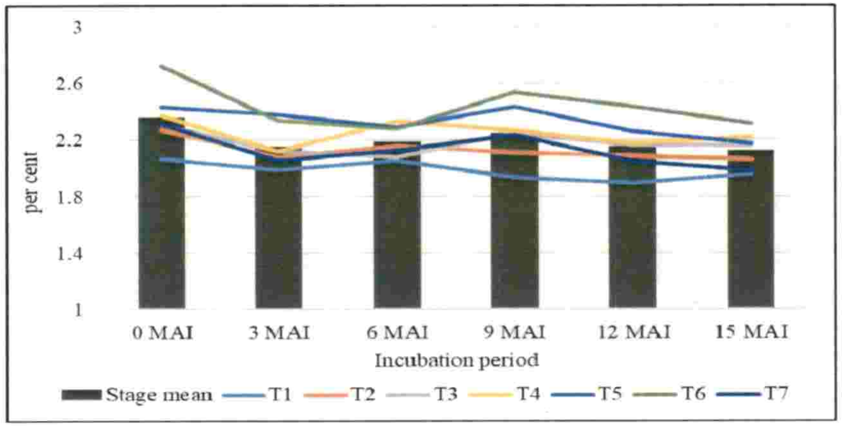

Fig. 9. Changes in the total carbon content (%) of soil at different stages of incubation

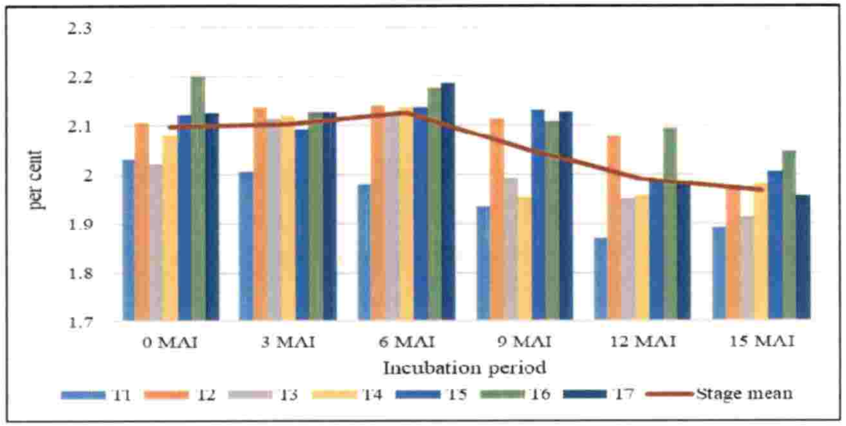

Fig. 10. Changes in the organic carbon content (%) of soil at different stages of incubation

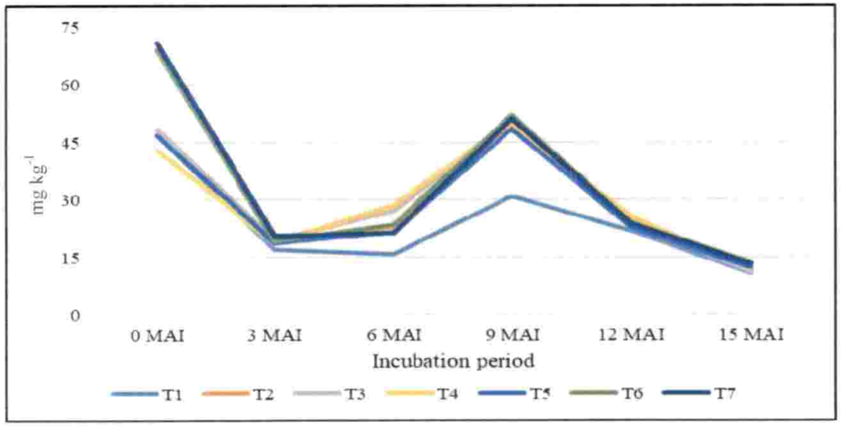

Fig. 11. Changes in the NH_4-N content (mg kg^{-1}) at different stages of incubation

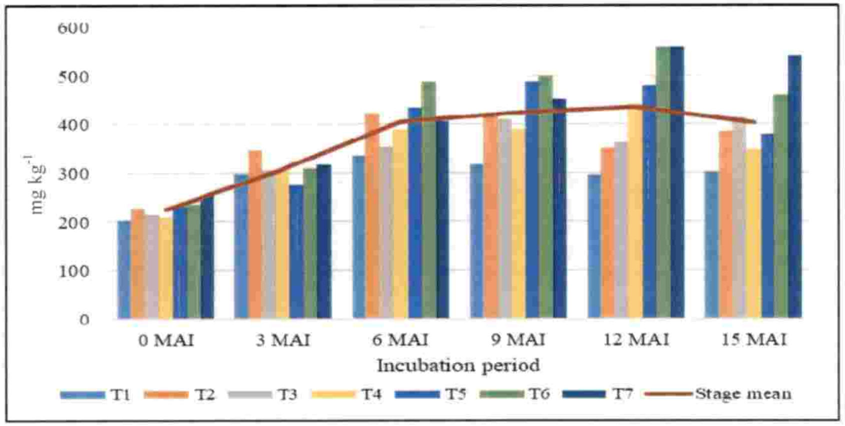

Fig. 12. Changes in the NO_3-N content (mg kg^{-1}) at different stages of incubation

Total carbon showed a positive correlation with carbon fractions namely HWSC, POXC and organic carbon and also with various nitrogen fractions like NH_4-N, THyN, $KMnO_4$-N and total N. The proven relationship between carbon and nitrogen in most of the soils hold good in the present study also as evidenced from the positive correlation noticed.

5.3.1.6. Organic carbon

Soil test based POP + biochar treatment recorded the highest organic carbon content throughout the incubation period, whereas the control recorded the lowest (Fig. 10). As in the case of total carbon, it is the carbonaceous nature of biochar that has brought about the increase in organic carbon content. Only a marginal increase could be noticed in the organic carbon content with increase in biochar levels, as against that in total carbon. This can be related to the low amount of chromic acid extractable carbon in biochar.

It was observed that with the advancement of incubation period, there was a decline in the organic carbon content, which was similar in all the treatments. The decrease could be attributed to the decomposition of added organic sources. In order to quantify the rate of decrease, simple regression analysis was resorted to. Here the highest rate of reduction was noticed in soil test based POP (4.177 mg kg^{-1} day^{-1}). With an increase in the biochar levels, sharp reduction was noticed in the rate of decrease. Applying biochar together with inorganic fertilizer sources further aggravated the reduction. A positive correlation existed between organic carbon and all other carbon fractions analysed. In case of nitrogen fractions, NH_4-N, THyN and total N alone maintained a positive relationship.

5.3.2. Dynamics of nitrogen

Nitrogen is one of the six macronutrients required for plants throughout and is vital as a major component of chlorophyll, the compound that helps to produce sugars from water and CO_2 in the presence of sunlight. More than 90 - 95 per cent of soil nitrogen is in organic form but the plant depends on the inorganic N sources though it accounts for only 5 - 10 per cent. Among the inorganic N forms, NO_3-N is the most abundant form in an aerobic environment and is taken by the root tissues through mass flow. Transformation of organic nitrogen plays decisive role in making available nitrogen for crop growth at the same time minimizing its losses. Dynamics of carbon and nitrogen are monitored to assess how the crop, its management practices and other inputs alter the ability of soil to store and cycle these nutrients. By enhancing the soil content of inorganic N forms, namely NH_4 and NO_3 through direct adsorption, reducing the losses of N through leaching and through N_2O emission and by increasing the population of nitrifying soil bacteria towards increased biological retention of N, the efficacy of biochar in controlling the rates of N cycle has been proved beyond doubt through research till date.

The treatment effect on the dynamics of N were assayed through an incubation experiment conducted for 15 months time. Here samples were drawn at 3 months interval and subjected to analysis on N fractions. Inorganic N fractions namely NH_4 and NO_3 and organic N fractions namely total hydrolysable N (THyN) and amino acid N (AAN) were estimated in the present study. In addition, $KMnO_4$-N and total N were also estimated.

5.3.2.1. Inorganic nitrogen

As against the control, NH_4-N fraction was higher in the treatments soil test based POP + biochar and soil test based POP, which were on par statistically. The highest value for NH_4-N (53.39 mg kg^{-1}) was registered during 0th month irrespective of treatments. With the progression of incubation, NH_4-N declined steadily at 3 MAI, then increased upto 9 months of incubation after which a decreasing trend could be noticed till the incubation ended. At all periods of incubation, treatments made a significant effect on NH_4-N content (Fig. 11). The fluctuation noticed with respect to the NH_4-N can be attributed to the increased adsorption of NH_4-N by biochar during the initial phase of experiment, followed by increased rate of mineralization leading to conversion of organic to inorganic form over time.

Adsorption of NH_4-N can be also related to the CEC of biochar. CEC of biochar used in the present study was 15.78 cmol (+) kg^{-1}, which shows that about 2880 positively charged NH_4-N can be adsorbed and retained by one kilogram of biochar material. Lehmann *et al.* (2006) have suggested that biochar can adsorb NH_4-N from the soil solution thus reducing NH_4-N at least temporarily, but perhaps concentrating it for microbial use. The reduction could be also due to the high C: N ratio as suggested by Lehmann *et al.* (2006). But it should be noted that immobilization associated with biochar additions to soil would be greatly limited by the recalcitrant nature of biochar (DeLuca and Aplet, 2007).

Quite contrary to NH_4-N, incubation had a significant effect in increasing NO_3-N content from 224.3 mg kg^{-1} (0 MAI) to 435.2 mg kg^{-1} (12 MAI). The treatment effect was similar as that of NH_4-N with soil test based POP + biochar and soil test based POP registering higher values, that were statistically comparable also (Fig. 12). The enhancement in NO_3-N is the direct effect of biochar and other organic and inorganic inputs in increasing the population of nitrifying organisms. This fully agrees with the findings of Shenbagavalli and Mahimairaja (2012), Dai *et al.* (2014) and Jha *et al.* (2016).

The daily release of NO_3-N was also quantified by simple regression analysis. The increase in release rate was maximum with soil test based POP (0.702 mg kg^{-1} day^{-1}). followed by soil test based POP + biochar (0.595 mg kg^{-1} day^{-1}). Further it was noticed that, the rate of release was minimal in control, which was totally devoid of any energy supplements. The rate of release of 0.446 mg kg^{-1} day^{-1}, in the biochar (10 t ha^{-1}) alone treatment got enhanced to 0.595 mg kg^{-1} day^{-1}, when soil test based POP was combined with biochar application.

5.3.2.2. Organic nitrogen

Organic nitrogen consists of THyN which is a mixture of NH_4, amino acid and hexosamine. In addition, it also contains some unaccounted fraction which cannot be hydrolyzed using 6 *M* HCl. This fraction is usually quantified mathematically on subtracting hydrolysable and inorganic N from the total N.

The treatments soil test based POP and soil test based POP + biochar were comparable in terms of THyN in registering higher values of 1499 and 1477 mg kg^{-1} respectively (Fig. 13). The positive effect of the two treatments on increasing THyN is due to promotional effect brought about by the organic sources namely biochar, FYM and urea. At all times control registered lowest value. Advancement in incubation had a favourable effect on THyN as reflected form the increase noticed

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upto 6 months of incubation, where the maximum value was recorded. A progressive decrease was noticed after 6 months and reached at 1215 mg kg^{-1} towards the end.

Numerous N compounds ranging from high molecular weight polyphenol bound N to low molecular weight amino acids makes the soil organic N, among which AAN occupies a major share. By virtue of its higher turnover rate when compared to the complex substrates, the soil amino acids are rapidly immobilized and mineralized by the soil microorganisms and thus serve as the important store house for immobilized N and a dominant transitional available form of N both for plants and soil biota (Lu *et al.*, 2018). In soil, amino acid N occurs in the form of protein in live microbial biomass.

Incubating the experimental soil with different treatments had a promising effect on AAN content which was highest with soil test based POP followed by soil test based POP + biochar, which were on par statistically. As always the control registered the lowest value (321.5 mg kg^{-1}), irrespective of incubation period. Advancement in incubation had a positive effect on this organic N fraction as evidenced from its increase upto 12 months of incubation. Though the content declined during 15 months of incubation, the reduction was not as much compared to initial value (Fig. 14). The rate of increase was the lowest in soil alone treatment throughout the period of incubation. The simultaneous presence of carbon from biochar and nitrogen from urea and biochar would have helped in the multiplication of microorganisms finally leading to the increased amount of AAN (in form of protein in live microbial biomass). The structural simplicity of amino acid is another reason for its better access by microorganisms.

5.3.2.3. Total nitrogen (Fig. 15)

Total N was lowest in the control at all stages of incubation, whereas, the treatments soil test based POP + biochar (2149 mg kg^{-1}), soil test based POP (2134 mg kg^{-1}), biochar 5 t ha^{-1} (2110 mg kg^{-1}) and FYM 10 t ha^{-1} (2108 mg kg^{-1}) were highest in terms of total N. Definite trend did not exist among the treatments within stage of incubation. With the advancement of incubation, the total N content decreased, though not significant. In comparison to the various N fractions the content of total N remained more or less constant throughout the incubation period.

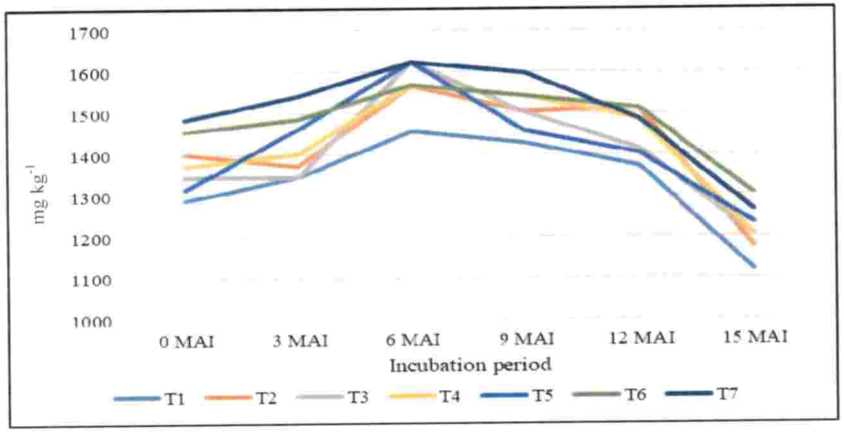

Fig. 13. Changes in the THyN content (mg kg^{-1}) at different stages of incubation

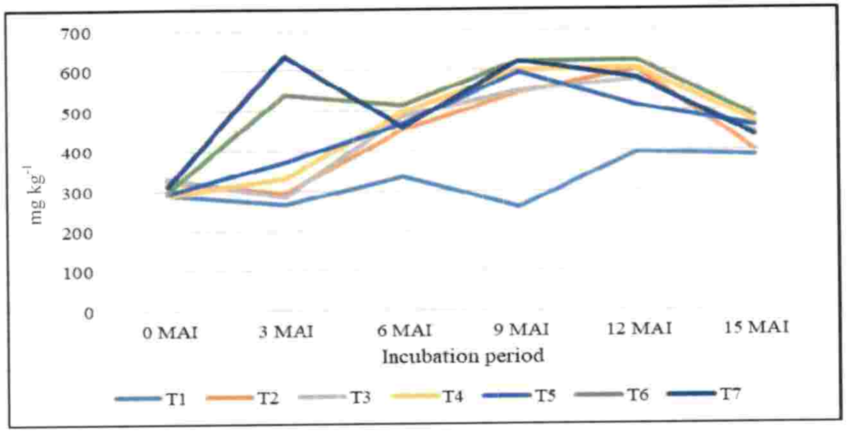

Fig. 14. Changes in the amino acid N content (mg kg^{-1}) at different stages of incubation

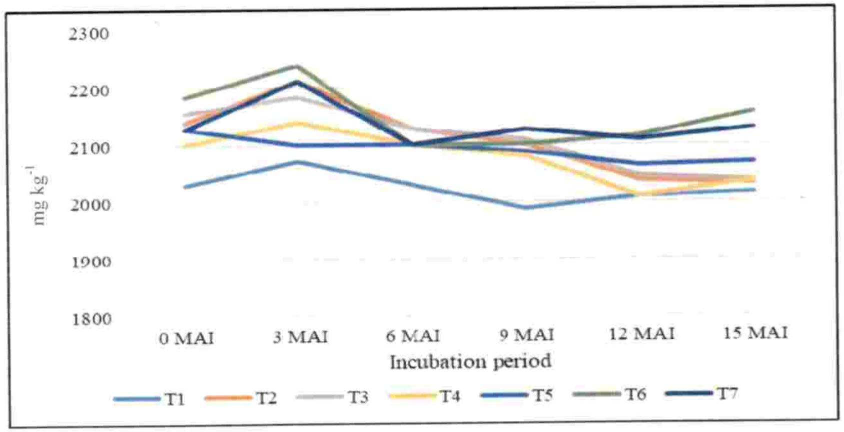

Fig. 15. Changes in the total N content (mg kg^{-1}) at different stages of incubation

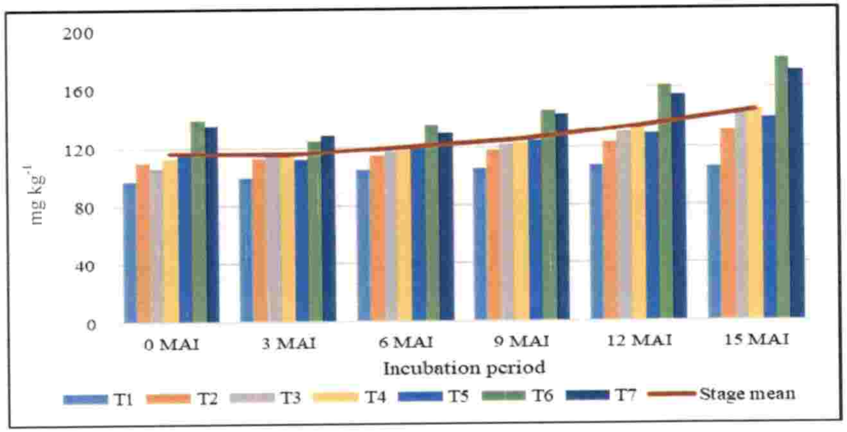

Fig. 16. Changes in the $KMnO_4$-N content (mg kg^{-1}) at different stages of incubation

Unlike the N fractions, the possibility of total N getting changed during incubation is limited, because of negligible losses through volatilization and leaching and which is also not easily altered by management practices.

5.3.2.4. $KMnO_4$-Nitrogen

The available N in soil refers to a fraction of the total N which is converted into forms accessible to plant. This constitutes only 0.5 to 2.5 per cent (rarely 5 %) of total N in soil at any given time. Alkaline $KMnO_4$ is a mild oxidizing agent and can extract out the easily hydrolysable and oxidizable fractions of organic N, simulating the mineralization and supply of N to the crop throughout the life cycle. Hence, this form of N is of great importance in crop growth and production.

The various treatments imposed brought about significant changes not only among themselves but also with the advancement in incubation period. Significantly highest value was associated with soil test based POP + biochar, followed by soil test based POP. With an increase in biochar levels, $KMnO_4$-N also increased though insignificant on statistical scrutiny (Fig. 16). Interaction between the treatments and stages of sampling proved positive and superior in respect of the treatment soil test based POP and soil test based POP + biochar application in yielding higher values for $KMnO_4$-N content. The soil alone treatment registered significantly lower $KMnO_4$-N at all stages of incubation.

The quantification on release rate of $KMnO_4$-N was done through simple regression analysis which revealed that the rate of release was maximum in soil test based POP + biochar, followed by soil test based POP. Application of biochar alone had reduced effect in the rate of release as against its application along with NPK. The richness of biochar in terms of carbon which act as the driving pool for microorganism along with the nutrients contained in the biochar and FYM is the reason for the enhancement in $KMnO_4$-N content in the treatments specified.

Simple correlations studies between different fractions of carbon and nitrogen revealed that among the carbon fractions the MBC and total carbon maintained positive relationship with $KMnO_4$-N, whereas WSC, HWSC and POXC had negative relationship with $KMnO_4$-N. Considering the N fractions, NO_3-N and AAN alone had a positive relationship with $KMnO_4$-N. All the fractions of C and N that showed correlation with $KMnO_4$-N were subjected to path analysis to segregate the direct and indirect effect.

Among the C fractions, the direct effect of MBC and total carbon on $KMnO_4$-N status was very high and positive, whereas the direct effect of WSC was negative but very high. MBC, which is the measure of C contained within the living component of SOM is an indicator of decomposition of SOM, releasing CO_2 and nutrients in plant available forms, especially N, P and S. This statement is fully supported from the positive high direct effect of MBC contained with $KMnO_4$-N on path analysis.

Further the path analysis data reinstates the role of AAN as a store house of immobilized N and available N form for plants and soil microorganisms. Inclusion of biochar alone at different levels *viz.* 5, 7.5 and 10 t ha^{-1} and along with NPK brought about an additional increase in the AAN status. It is the AAN which further mineralize to form other inorganic fractions like NH_4 and NO_3, which are the plant usable forms. The biochar addition to soil caused reduction in ammonification compared to the control due to adsorption and reduce the potential for NH_3 volatilization. The overall effect is the increased available N content followed biochar application. The encouraging effect of biochar on $KMnO_4$-N was further confirmed through path analysis, wherein the direct effect of NO_3-N on $KMnO_4$-N was very high and positive. The contribution of AAN directly was low, whereas, its indirect effect through NO_3-N was positive and very high.

5.3.3. Maximum water holding capacity

The soil act as a sponge to absorb and retain water and it is the pore space which serve as the conduit which allows water to infiltrate and percolate. The soil and plant growth depends on the water content because it serves as the solvent and carrier of nutrients for plant growth besides itself acting as a nutrient. This indicates the relevance of soil's capacity to hold water, retain it and regulate its release for plant utilization. In general, biochar has a very high water holding capacity which was true in the present experiment also, where the produced biochar recorded maximum a WHC of 307.7 per cent.

The water holding nature of biochar was estimated in the incubation experiment also, wherein the treatment biochar 10 t ha^{-1} recorded the highest MWHC of 36.02 per cent, followed by soil test based POP + biochar (35.75 %) as against 33.31 per cent recorded in the soil alone treatment. At all stages of incubation, the superiority of biochar 10 t ha^{-1} and soil test based POP + biochar was prominent. MWHC was lower in soil alone treatment at all stages of incubation. It was further noticed that with increase in biochar level, MWHC also showed an increase (Fig. 17). Changes in the MWHC of the soil was primarily responsible for the water holding capacity of the added biochar (307.7 %). The increase in particle surface area and the porous structure of biochar were stated responsible for the increase in the WHC of soil consequent to biochar application (Lehmann *et al.*, 2003). The formation of humic substance in soil following biochar application is another reason for the increased WHC as reported by Piccolo *et al.* (1996). The hydrophilic functional groups present on the surface of the graphene sheet of the biochar facilitates the increase in water retention capacity of the soil.

5.4. Field experiment

For evaluating the potency of biochar on soil properties, growth, yield, quality and nutrient uptake, field experiment was conducted with Chinese potato as the test crop followed by vegetable cowpea, after which the residual effect of biochar was assessed. The results obtained are substantiated in the light of supporting evidences.

5.4.1. Direct and residual effect of biochar on post-harvest soil properties

5.4.1.1. Soil reaction

Soil reaction or pH, an important electro-chemical property is a key factor that decides availability of various nutrients and also the microbial activity that governs the decomposition of organic matter and nutrient release. Many factors influence soil pH namely the parent material, precipitation, native vegetation, crop grown, irrigation water, burning fossil fuels and application of fertilizers that lead to residual acidity and also organic manures / amendments. The changes in soil pH that results from the application of any input is worth estimating. The difference in pH brought about by biochar application was studied under field condition. The pH increased to 5.95 from the initial value of 5.24 in the treatment biochar 10 t ha^{-1}. The same treatment maintained superiority in both the test crops (Fig. 18). The profound influence of biochar on soil pH has been thoroughly researched upon by many scientists. The increased concentration of alkaline metal oxides (Ca, Mg and K^+) contained in the biochar and also the reduced concentration of soluble soil Al^{3+} (Steiner *et al.*, 2007), the high liming potential of biochar that raises the pH of the highly weathered soil (Jien and Wang, 2013; Dainy, 2015) and also the typically alkaline nature of biochar itself (Shenbagavalli and Mahimairaja, 2012; Elangovan, 2014; Akshatha, 2015; Dainy, 2015) are the probable reasons pointed out behind the increase in pH following biochar application. Several researchers from their works on biochar reported that, when biochar is applied, the CEC of soil gets increased which would give a chance for Al and Fe to get bound with the soil exchange sites, leading to a reduction in exchangeable Al and soluble Fe in soils, which fully agrees with the findings of the present study also. The association of functional groups such as -COO- (-COOH) and -O- (-OH) contained in the biochar with H^+ also contributed considerably to the alkalinity as suggested by Yuan *et al.* (2011). This was further conclusively proved through the FT-IR data (Fig. 2)

The process of pyrolysis that yields biochar is an alternate route to form alkaline oxides or carbonates, which on getting released into the environment reacts with H^+ and monomeric Al^{3+} decreasing the exchangeable acidity thus raising the soil pH (Novak *et al.*, 2009). Calcium replaces monomeric Al^{3+} species on the soil exchange sites and generates alkalinity. Subsequently there is an increase in soil solution pH as a result of the reduction of readily hydrolysable monomeric Al^{3+} and the subsequent formation of the neutral $[Al(OH_3)]$ species (Sparks, 2003). According to Chan and Xu (2009), the high concentration of carbonates in biochar was another reason for the liming properties noticed.

5.4.1.2. Electrical conductivity

In soil system, EC is a measure of its salinity and serves as an important indicator of soil health. The role of biochar on soil EC was studied considering its importance for plant growth and production. In the present study it was found that EC increased in the experimental soil on applying specified treatments. Soil test based POP + biochar registered the highest EC value of 0.084 dS m^{-1}, followed by soil test based POP alone (Fig. 19). The increase in soluble salt content of soil might be due to the higher proportion of soluble salts added through biochar leading to an increase in electrolytes content resulting in an increase in soil EC. Biochar produced in the present study recorded an EC of 3.42 dS m^{-1}. The finding of this investigation synchronizes with that of Nigussie *et al.* (2012), Shenbagavalli and Mahimairaja (2012), Elangovan (2014), Akshatha (2015) and Dainy (2015). Another possible reason for the increased EC might be due to the release of cations and anions which are loosely bound with biochar into the soil solution making it available for plant growth (Glaser *et al.*, 2002; Gundale and DeLuca, 2006; Chan *et al.*, 2008).

5.4.1.3. Organic carbon

Treatments imposed a significant influence on chromic acid oxidizable carbon of the post-harvest experimental soil which increased from 1.55 per cent in the beginning of experiment to 1.778 per cent after the first crop and to 1.767 per cent after the second crop. In both the main and succeeding crop, application of biochar 10 t ha^{-1} either alone or in combination with soil test based POP showed a superior effect by registering significantly higher organic carbon values. With an increase in levels of biochar, significant increase in organic carbon was noticed and the trend was similar in the case of residual effect also (Fig. 20). The positive effect of biochar on SOC is primarily due to the high amount of carbon contained in biochar (64.14 %). In addition, the existence of recalcitrant organic carbon in biochar also add on to the SOC level (Nigussie *et al.*, 2012). Another highlight on soil organic carbon data of the present experiment is that there was no significant reduction even after the second crop of vegetable cowpea. This might be due to the highly persistent nature of biochar in soil than any other form of organic manure which makes it classic for sequestering carbon. Ample research findings support the data on organic carbon as acquired in this present investigation.

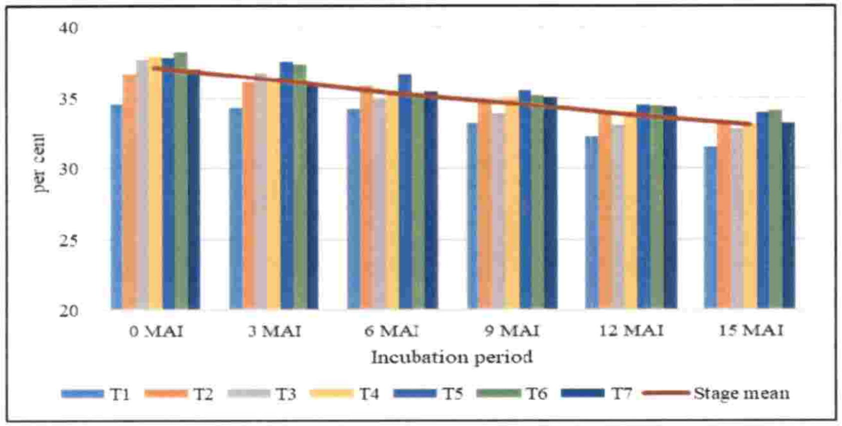

Fig. 17. Changes in the maximum water holding capacity (%) at different stages of incubation

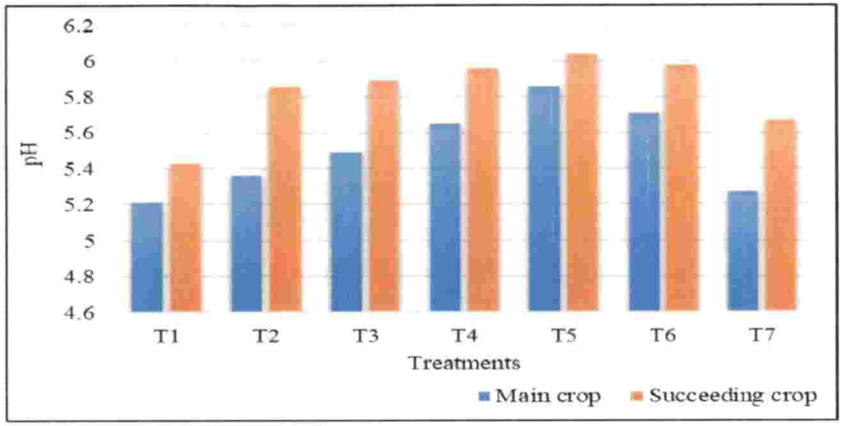

Fig. 18. pH of post-harvest soil as influenced by the biochar application

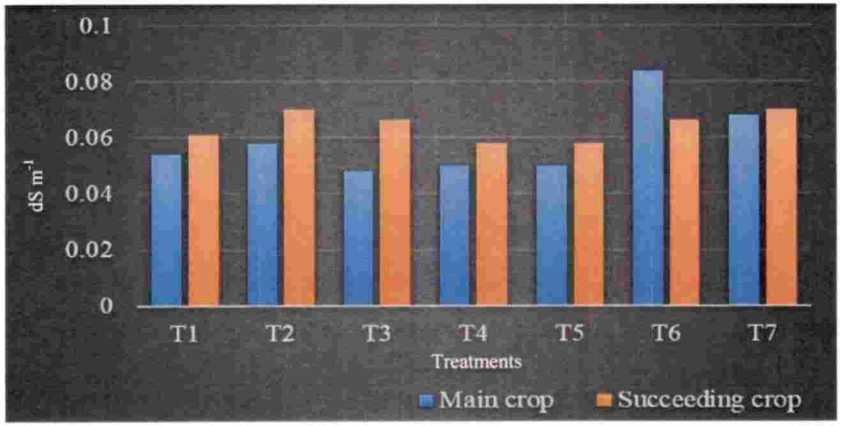

Fig. 19. Electrical conductivity (dS m^{-1}) of post-harvest soil as influenced by the biochar application

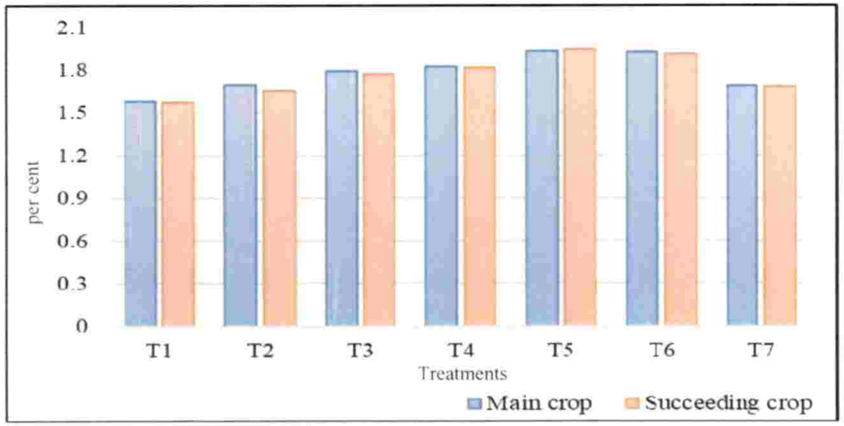

Fig. 20. Organic carbon content (%) of post-harvest soil as influenced by the biochar application

5.4.1.4. Exchangeable acidity

The amount of acid cations (Al^{3+} and H^{+}) occupied on the exchange sites is called as exchangeable acidity and it is measured by titrating the 0.1 *M* KCl extract to a phenolphthalein endpoint at pH 8.3. The results revealed that exchangeable acidity was highest for the treatment soil test based POP (0.093 meq $100g^{-1}$) (Table 37) followed by the control, whereas it was lowest in case of biochar 10 t ha^{-1}, both after Chinese potato and vegetable cowpea (Fig. 21).

Another noticeable feature was the marginal reduction in exchangeable acidity with an increase in the biochar application rate. Besides increase in soil pH, incorporation of biochar helped to release base cations into an acidic soil which can participate in exchange reactions replacing exchangeable Al^{3+} and H^{+} on the soil surface thus bringing a decrease in exchangeable acidity, which fully corresponds with the findings of Warnock *et al.* (2007), Steiner *et al.* (2007), Chan *et al.* (2008), Novak *et al.* (2009) and Yuan *et al.* (2011). Application of 10 t of biochar per hectare reduced exchangeable acidity from 0.087 to 0.050 meq $100g^{-1}$ owing to the reduction in exchangeable Al^{3+}. Similar findings were also put forth by Abewa *et al.* (2014) on applying 12 t h^{-1} of eucalyptus biochar in an acidic soil of Northwestern Ethiopia. The increase in pH of post-harvest soil in the present investigation further adds support for the above findings.

5.4.1.5. Availability of nutrients

Availability of plant nutrients is strongly related to the soil properties, wherein the high content of organic carbon and CEC escalates the soils capacity to hold the essential plant nutrients in sufficient amounts so as to meet the nutrient requirement of crops. Both SOC and CEC improvement could be attained through the incorporation of organic manures like biochar which would eventually bring changes in nutrient availability. Biochar with its high CEC favours the nutrient fixation and release through ion exchange reaction besides acting as a nutrient reservoir. On the whole biochar affects the soil nutrient availability mainly through two ways *viz.* nutrient retention and nutrient addition. The discussion herewith relates to the role of biochar in bringing out a favourable effect on nutrient availability.

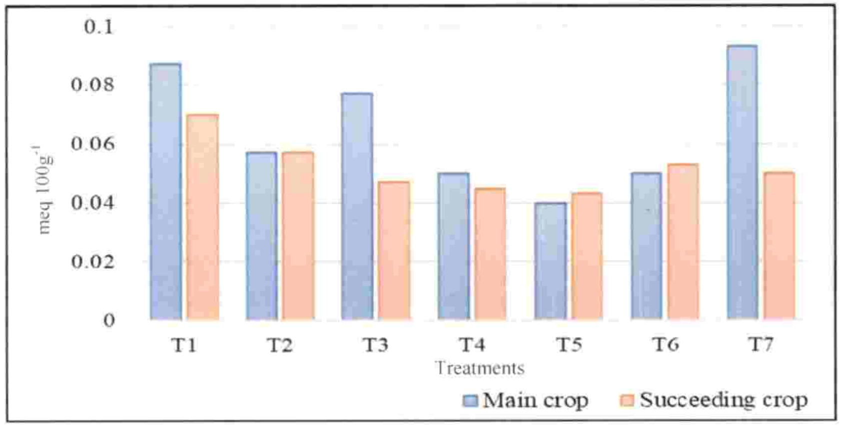

Fig. 21. Exchangeable acidity (meq $100g^{-1}$) of post-harvest soil as influenced by the biochar application

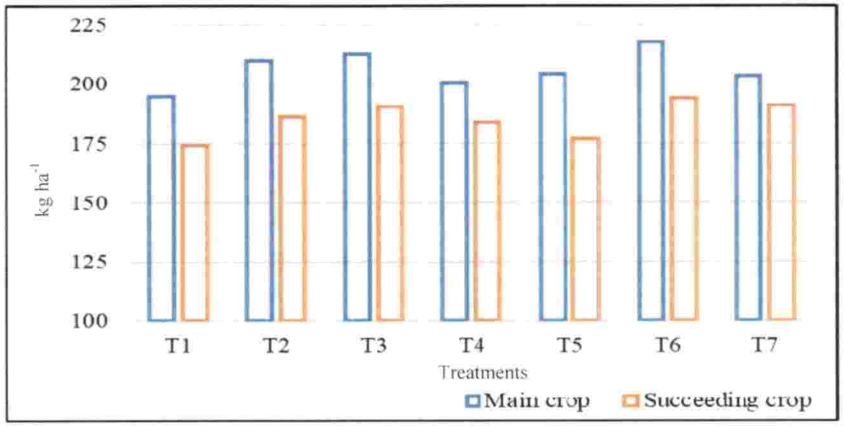

Fig. 22. $KMnO_4$-N status (kg ha^{-1}) of post-harvest soil as influenced by the biochar application

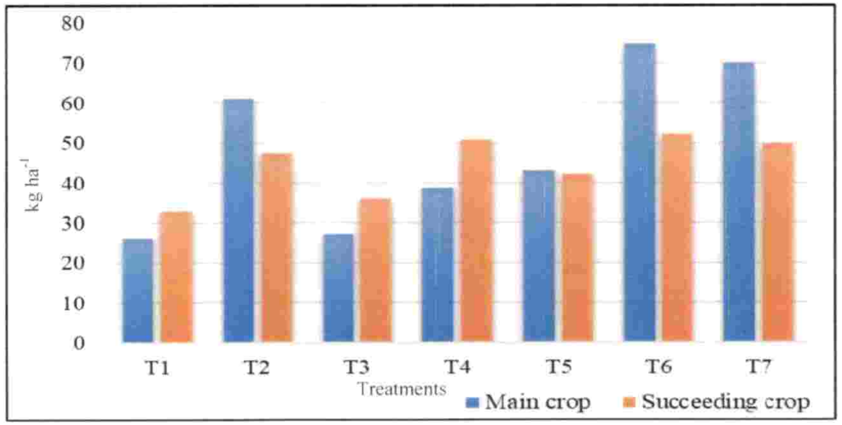

Fig. 23. Bray-P status (kg ha^{-1}) of post-harvest soil as influenced by the biochar application

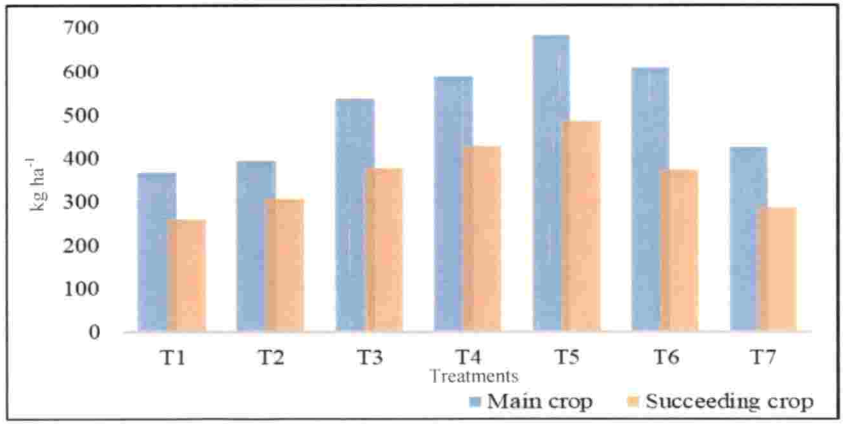

Fig. 24. NH_4OAc-K status (kg ha^{-1}) of post-harvest soil as influenced by the biochar application

5.4.1.5.1. $KMnO_4$-N

In both the seasons soil test based POP + biochar recorded higher values for $KMnO_4$-N, but the effect was on par with biochar 5 t ha^{-1} after the first season and with biochar 5 t ha^{-1} and soil test based POP after succeeding crop. Control always registered lowest value of $KMnO_4$-N (Fig. 22). The soil status of $KMnO_4$-N was less after second crop of vegetable cowpea which is purely because the crop was not nourished with nutrients neither organic nor inorganic. The increased availability of N is attributed to the nutrient addition from biochar and inorganic sources and also from the possible reduction in leaching losses due to the highly adsorptive nature of biochar. The higher CEC and surface area of added biochar would also have improved the adsorption of NH_4^+. Similar results were reported from the studies of Yao *et al.* (2012), Elangovan (2014), Sika and Hardie (2014) and Dainy (2015) on working with efficacy of biochar. Generally, the plant based biochar consists of many N containing structures *viz.* amino acids, amines and amino sugars which on pyrolysis gets condensed to form heterocyclic N aromatic structures (Cao and Haris, 2010). According to Gaskin *et al.* (2010), the aromatic N structures are not plant available and are considered as recalcitrant heterocyclic N rather than bioavailable amine N (Novak *et al.*, 2009; Cao and Haris, 2010). Application of biochar along with inorganic N fertilizers is found to have a stimulating effect on making available the unavailable recalcitrant N. In other words, this shows the potential of biochar in increasing the efficiency of inorganic N sources. These findings confirm fully with the results of the present investigation in which the treatment soil test based POP + biochar registered the all-time high value in respect of $KMnO_4$-N.

5.4.1.5.2. Bray-P

In both the seasons, Bray-P content of soil increased in all the treatments in comparison with the initial value (27.08 kg ha^{-1}) (Fig. 23). In the post-harvest soil of main crop, soil test based POP + biochar (74.79 kg ha^{-1}) registered higher value however it was on par with soil test based POP (70.10 kg ha^{-1}) and FYM 10 t ha^{-1} (61.34 kg ha^{-1}). Similarly, in the succeeding crop also the same treatment showed superiority in registering higher values, but the effect was comparable with biochar 10 t ha^{-1} (50.78 kg ha^{-1}), soil test based POP (49.91 kg ha^{-1}) and FYM 10 t ha^{-1}

(47.46 kg ha^{-1}). In both experiments, the lowest value was in control. Irrespective of the treatments the availability of P was more during the first crop. The possible mechanisms for increased P availability with biochar application in soil are the presence of soluble and exchangeable PO_4^{3-} in biochar, modification of soil pH, complex formation with Fe and Al ions, promotion of microbial activity which hastens P mineralization *etc.* according to Novak *et al.* (2009), Laird *et al.* (2010), Hass *et al.* (2012) and Parvage *et al.* (2013). It can further be explained that, with the application of biochar the liming effect that follows lead to precipitation of Al and Fe as $Fe(OH)_3$ and $Al(OH)_3$, which increases P availability in the soil system (Ch'ng *et al.*, 2014; Dainy, 2015).

The negative charges in biochar are likely to have blocked the fixation sites of P in the soil and / or complexed with Fe and Al in the soil solution, thereby increasing the P activity in soil solution. This is true in the lateritic soils of Kerala containing predominant amount of Fe and Al in the soil solution. The increased availability of P after application of biochar could be due to the direct nutrient addition by the material itself (0.982 % P in biochar) and changes in soil microbial dynamics. Similar release pattern was also reported by Lehmann *et al.* (2006), Lehmann and Rondon (2006) and Chan *et al.* (2007).

5.4.1.5.3. NH_4OAc extractable K, Ca and Mg

The content of alkaline earth metals namely K, Ca and Mg, extracted using ammonium acetate increased during the experimental period with the application of different treatments. While the K content was higher with the application of biochar 10 t ha^{-1}, the Ca and Mg content was more with soil test based POP + biochar. Levels of biochar had a significant effect on increasing K content. On analysing the effect of biochar on Ca and Mg separately, it could be seen that the treatments soil test based POP + biochar, biochar 10 t ha^{-1}, FYM 10 t ha^{-1} and soil test based POP had a comparable effect on Ca. With respect to Mg, soil test based POP + biochar, FYM 10 t ha^{-1} (70.22 mg kg^{-1}) and soil test based POP (67.62 mg kg^{-1}) showed comparable effect. Content of Ca and Mg increased both after Chinese potato and vegetable cowpea, whereas the content of K increased only in the first season after which it decreased (Fig. 24, 25 and 26).

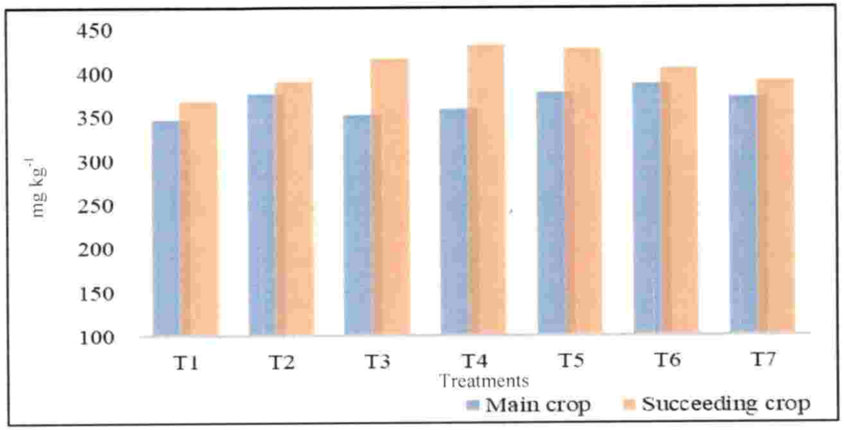

Fig. 25. NH_4OAc-Ca status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

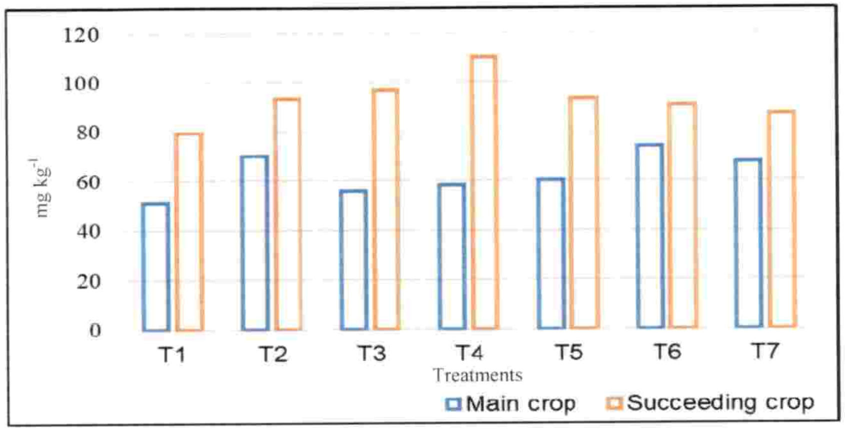

Fig. 26. NH_4OAc-Mg status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

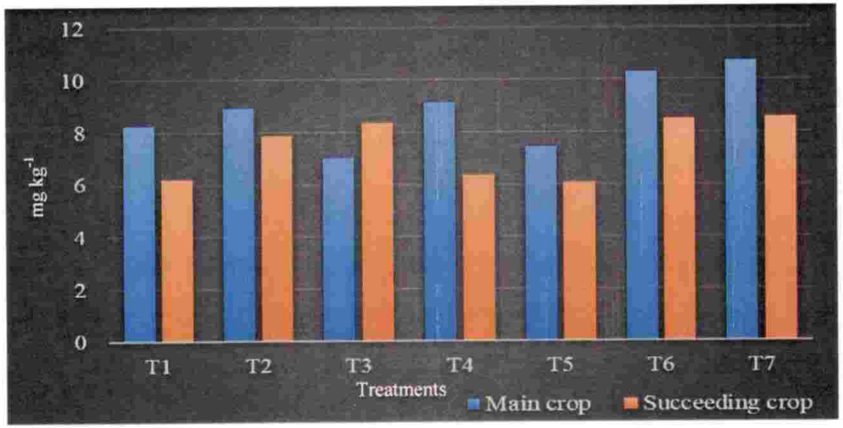

Fig. 27. $CaCl_2$-S status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

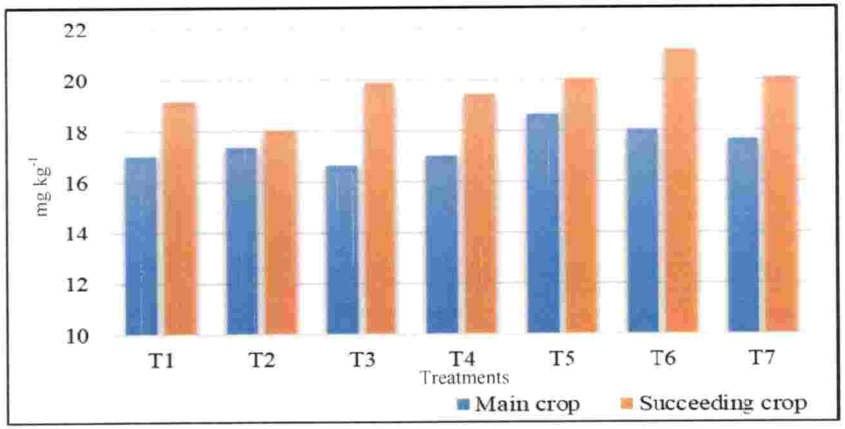

Fig. 28. HCl-Fe status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

The base cations contained in biochar exchanged with Al^{3+} and H^{+} making the soil enriched in terms of exchangeable base cations. In addition, the relatively high content of K (4.175 %), Ca (1.19 %) and Mg (0.456 %) in biochar and its ability to sorb considerable amount of base cations from soil solution lead to decreased leaching losses of K, Ca and Mg, thus making them more available. Unlike Ca and Mg, the reduction noticed after crop harvest in case of available K is due to the luxury consumption associated with this nutrient element.

5.4.1.5.4. $CaCl_2$-S

The results revealed the promotional effect of soil test based POP and soil test based POP + biochar on $CaCl_2$ extractable S. However, biochar alone did not have any significance on increasing $CaCl_2$-S status. Both the direct and residual effect of treatments were similar in terms of $CaCl_2$-S content (Fig. 27). The results suggested the improvement in S status following the application of fertilizers, organics and biochar which mainly is due to mineralization of organic forms of S brought about by the improvement in microbial activity. This is in concurrence with the findings of DeLuca *et al*. (2009), Elangovan (2014), Akshatha (2015) and Dainy (2015).

5.4.1.5.5. HCl extractable micronutrients

The effect of different treatments on HCl-Fe was only comparable. However, application of biochar 10 t ha^{-1} and soil test based POP + biochar recorded numerically higher values in the main and succeeding crop, respectively (Fig. 28). In terms of HCl-Mn, it was found to be higher in the treatment biochar 10 t ha^{-1} (44.56 mg kg^{-1}), which was comparable with all other treatments. The lowest value was in absolute control (35.26 mg kg^{-1}). In the succeeding crop, significantly lowest amount of HCl-Mn was recorded by the treatment biochar 10 t ha^{-1} (36.55 mg kg^{-1}), which in fact was the one that showed highest HCl-Mn content during the main crop (Fig. 29).

HCl extractable Zn was the highest in treatment soil test based POP + biochar, which was on par with FYM 10 t ha^{-1} (6.843 mg kg^{-1}) after the main crop. There was only marginal effect after the second crop. With an increase in biochar levels, the HCl-Zn increased, though only marginally (Fig. 30).

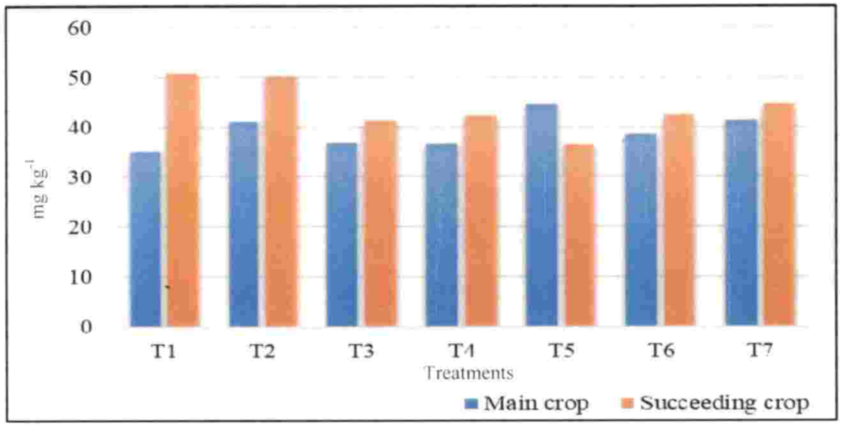

Fig. 29. HCl-Mn status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

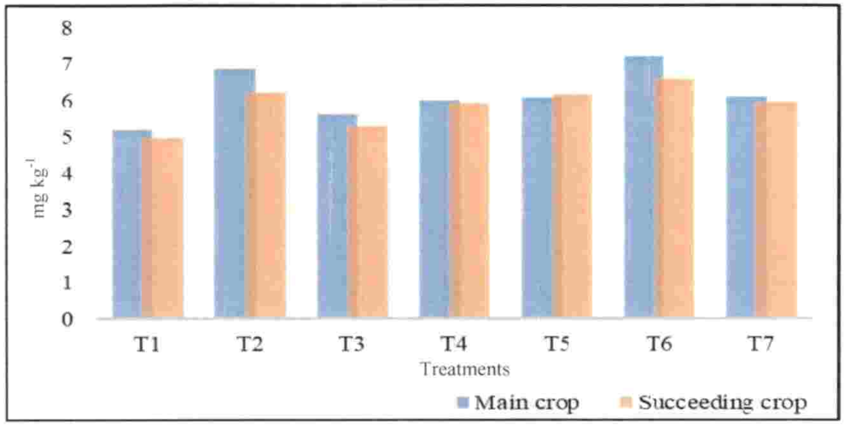

Fig. 30. HCl-Zn status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

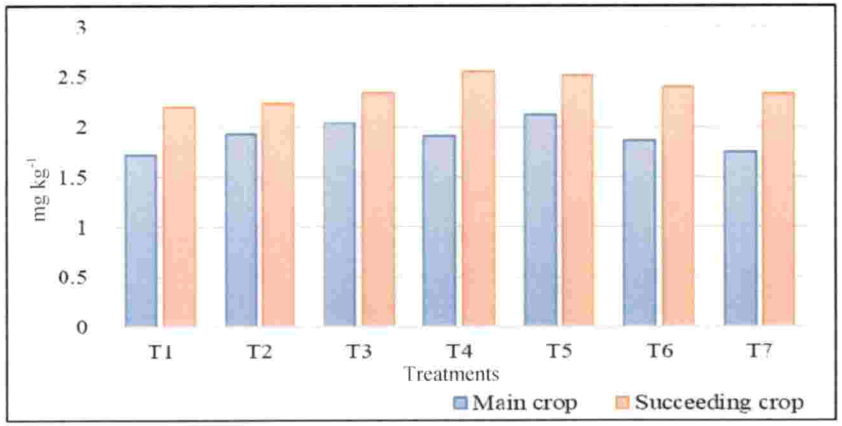

Fig. 31. HCl-Cu status (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

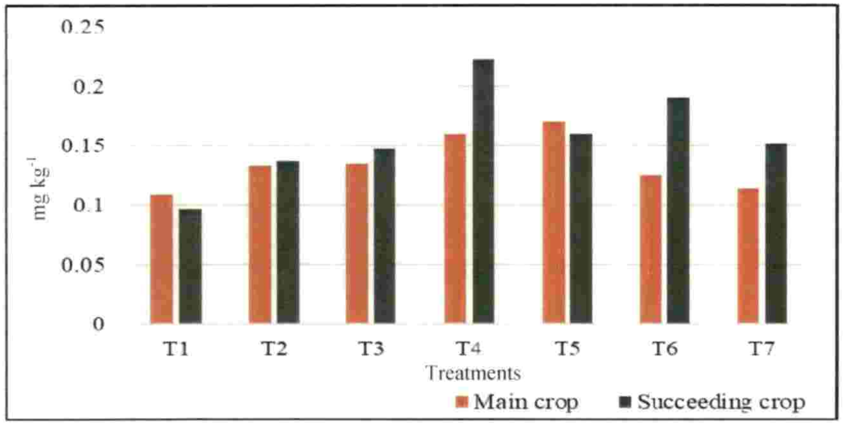

Fig. 32. Hot water soluble B content (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

The HCl-Cu content was highest in the treatment biochar 10 t ha^{-1} during the main crop and biochar 7.5 t ha^{-1} after the next crop, followed by rest of the treatments which were comparable with each other (Fig. 31). Control recorded the lowest value for Zn and Cu. HCl extractable Fe, Mn and Cu showed an increasing trend throughout the experiment, whereas the Zn content increased during the first crop and decreased thereafter. The encouraging effect of all the micronutrients experimented is due to the fact that the coconut based biochar grown under acidic soils is a rich source of these micronutrients. Similar results were also reported by Akshatha (2015) and Dainy (2015).

5.4.1.5.6. Hot water soluble boron

The treatments biochar 10 t ha^{-1} and biochar 7.5 t ha^{-1} registered higher values for hot water soluble B during the main crop, whereas in the ensuing crop biochar 7.5 t ha^{-1} and soil test based POP + biochar recorded higher values. Irrespective of treatments, the hot water soluble B increased significantly after the succeeding crop (Fig. 32). Little amount of boron contained in the coconut based biochar would have helped in its release to soil solution.

5.4.1.6. Microbial biomass carbon

The effect of different treatments, except control on MBC content was only comparable during the first season whereas in the second season the treatments soil test based POP and biochar 5 t ha^{-1} showed a significant increase. Control plots recorded lowest MBC (Fig. 33). The explanations under section 5.3.1.4 holds good here also.

5.4.1.7. Dehydrogenase activity

Dehydrogenase, strictly an intracellular enzyme is taken as an index for evaluating microbial activity. It plays an indispensable role in biological oxidation of organic compounds in soil and in turn reflects the total microbial population. Being a source of carbon and other nutrients, biochar influences the microbial population and hence the dehydrogenase activity. This is well established in the present study conducted in a lateritic soil.

Application of soil test based POP + biochar and biochar 10 t ha^{-1} were found to increase the dehydrogenase activity of post-harvest soil during the first experiment and the effect was comparable. However, in the post-harvest soil of succeeding crop, the treatment soil test based POP + biochar showed superiority by registering higher dehydrogenase activity (163.6 μg TPF g^{-1} soil $24hr^{-1}$). In both experiments, significantly lowest value was associated with control (Fig. 34). It was also noticed that the dehydrogenase activity increased with increase in biochar application rate, though the increase was only marginal. On comparing the sole application of biochar and fertilizer with their combined application, it was found that the dehydrogenase activity got enhanced to 163.6 μg TPF g^{-1} soil $24hr^{-1}$ than the sole application of biochar 10 t ha^{-1} (93.12 μg TPF g^{-1} soil $24hr^{-1}$) and soil test based POP (116.1 μg TPF g^{-1} soil $24hr^{-1}$), conveying the merits of conjoint use of organic and inorganic sources.

Adequate availability of both C and N that resulted from the combined application of NPK and biochar to the soil microbes might be the reason for the increase in their population and in turn the dehydrogenase activity. Similar observations with NPK + biochar application were also reported by Shenbagavalli and Mahimairaja (2012), Ameloot *et al.* (2013) and Demise *et al.* (2014). Significant and positive correlation of dehydrogenase activity with organic carbon, $KMNO_4$-N and MBC observed in the present study further strengthens the results.

Demise *et al.* (2014) was of the opinion that dehydrogenase activity can successfully be used as a parameter for evaluation of degree of recovery of degraded soils, where increase in enzyme activity indicated the improvement brought about by biochar. In the present study also the changes in dehydrogenase activity could be related to the soil property enhancement through biochar application. Positive relationship obtained between the dehydrogenase activity and soil properties supplements the above interpretation fully.

5.4.1.8. Cation exchange capacity

Of the several soil characteristics, the cation exchange capacity is the prime factor that governs its nutrient supplying power. For that reason, any factor influencing CEC will eventually influence the nutrient supplying power of the soil also. In the present study, various treatments tried had a significant influence on CEC (Fig. 35). The effect on registering higher CEC values was shared by the treatments that contained high quantity of biochar *viz.* soil test based POP + biochar, biochar 10 t ha^{-1} and biochar 7.5 t ha^{-1}. Increasing levels of biochar also increased the CEC. As could be expected lowest CEC was associated with control treatment.

The increase in CEC following biochar application can primarily be attributed to its high CEC [15.78 cmol (+) kg^{-1}], high specific surface area, high surface negative charge and charge density, as opined by several researchers from their works on biochar. In addition, the slow oxidation of biochar resulted in an increase in number of carboxylic and phenolic functional groups which finally increased the CEC of amended soil. This statement is strongly supported by the FT-IR (Fig. 2) and Raman spectrum (Fig. 3) of biochar, which exhibited the presence of carboxylic and phenolic groups in the biochar produced from coconut shell and husk.

Another reason for increase in the soil CEC is the increase in the pH dependant charges that resulted from the increase in pH of the respective treatments. This is in accordance with the findings of Jien and Wang (2013) who observed an improvement in soil CEC from 7.41 to 10.8 cmol (+) kg^{-1}, where pH increased from 3.9 to 5.1 with the application of 2 and 5 per cent biochar, to an acidic Ultisol. Similar observation was also noticed by vanZwieten *et al.* (2010) in a Ferralsol soil conducted under greenhouse condition. Increase in CEC with the application of biochar was also reported by Liang *et al.* (2006), Lehmann (2007), Chan *et al.* (2008), Robert and Taylor (2010), Shenbagavalli and Mahimairaja (2012), Elangovan (2014), Dainy (2015) and Rajalekshmi (2018).

5.4.1.9. Water holding capacity

As in the case of incubation experiment, in field experiment also the biochar exhibited promotional effect on MWHC of soil, wherein the treatments biochar 10 t ha^{-1} and soil test based POP + biochar recorded higher values. The reason for increase in MWHC following biochar application has been already discussed under the section 5.3.3.

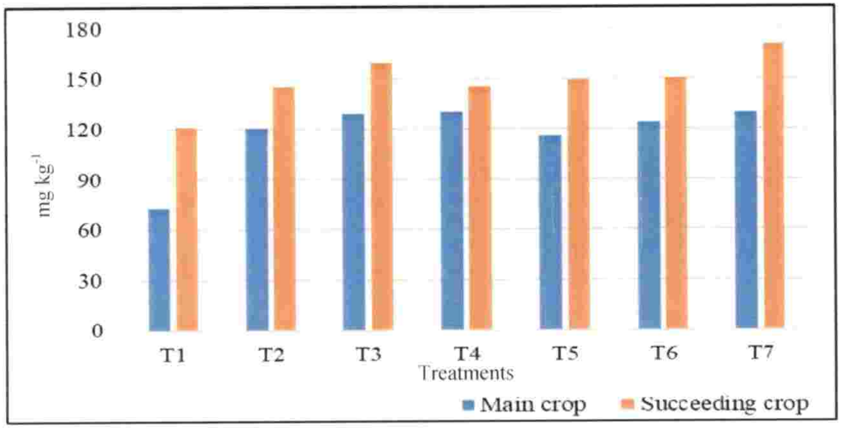

Fig. 33. MBC content (mg kg^{-1}) of post-harvest soil as influenced by the biochar application

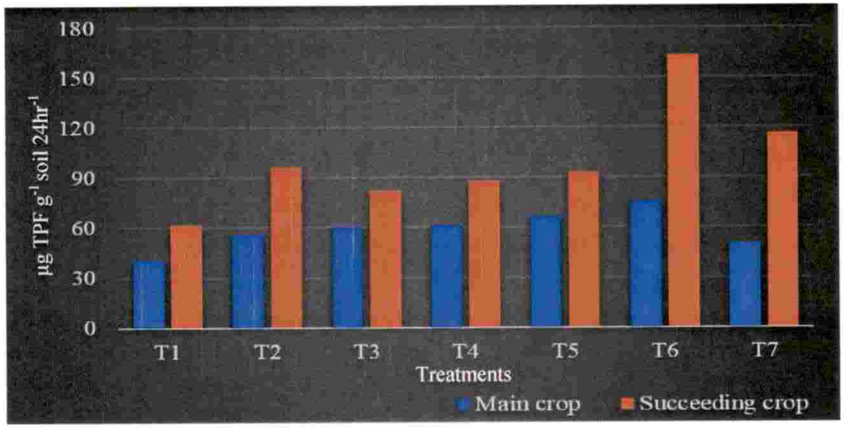

Fig. 34. Dehydrogenase activity (µg TPF g^{-1} soil 24hr^{-1}) of post-harvest soil as influenced by the biochar application

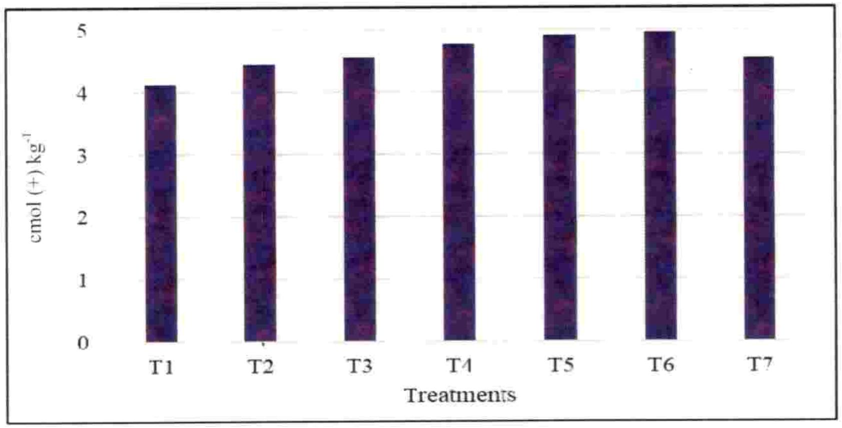

Fig. 35. Cation exchange capacity (cmol (+) kg^{-1}) of post-harvest soil as influenced by the biochar application

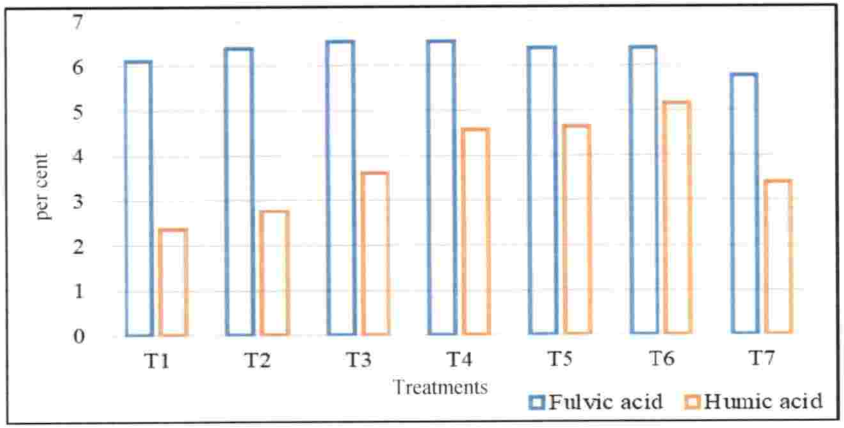

Fig. 36. Effect of biochar application on fraction of organic matter (%) in post-harvest soil

5.4.1.10. Fraction of organic matter

Humus, the older, decayed organic compound that have resisted decomposition makes up more than 50 per cent of SOM. This complex substance is found naturally in soil and it affects soil properties and plant physiological properties due to carboxylic and phenolic groups that it holds. It also improves soil aggregation, structure, water permeability, air flow, fertility, MWHC, microbial activity and CEC. The dominant fraction of humus are humic acid and fulvic acid. Since the biochar is a source of recalcitrant carbon, its effect on the fraction of organic matter was felt worth investigating.

The treatments which contained biochar in it and the treatment FYM 10 t ha^{-1} had a comparable effect on fulvic acid content. In the case of humic acid fraction, application of graded levels of biochar *viz.* 7.5 and 10 t ha^{-1} and its integration with soil test based POP increased its content (Fig. 36). The results reflected that large amount of C got sequestered in the soil due to application of biochar. Similar was the findings of Shenbagavalli and Mahimairaja (2012).

5.4.2. Direct and residual effect of biochar on growth components and yield

Plant height, average tuber girth, DMP, yield per plant and tuber yield were accounted towards interpreting the direct effect of biochar on Chinese potato. The treatment soil test based POP recorded the highest values for plant height (72.66 cm), average tuber girth (3.37 cm) and DMP (2959.3 kg ha^{-1}) which was comparable with soil test based POP + biochar. Whereas, in terms of per plant yield and tuber yield per hectare the treatment soil test based POP + biochar registered the highest values of 147.98 g and 24.04 t ha^{-1}, respectively as against the control values of 58.79 g and 16.62 t ha^{-1} each in terms of per plant yield and tuber yield (Fig. 37, 39 and 40).

The marked effect of biochar on crop yield increase is the consequence of soil fertility improvement in terms of physical properties (Bulk density, porosity and water holding capacity) (Chan *et al.*, 2008), chemical properties (pH and OC) (Liang *et al.*, 2006; Chan *et al.*, 2007) and biological properties (Enzyme activity) (Warnock *et al.*, 2007).

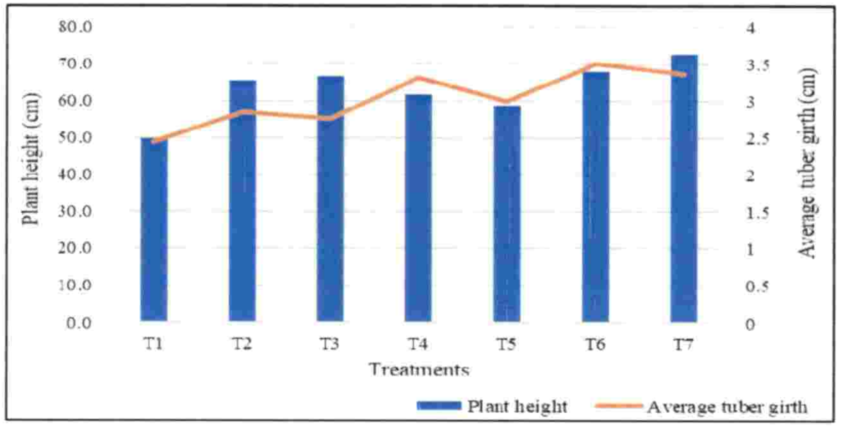

Fig. 37. Direct effect of biochar on growth components of Chinese potato

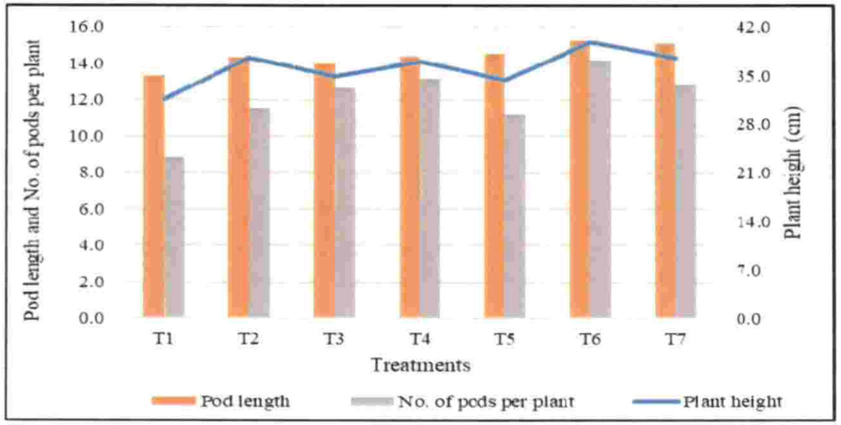

Fig. 38. Residual effect of biochar on growth components of cowpea

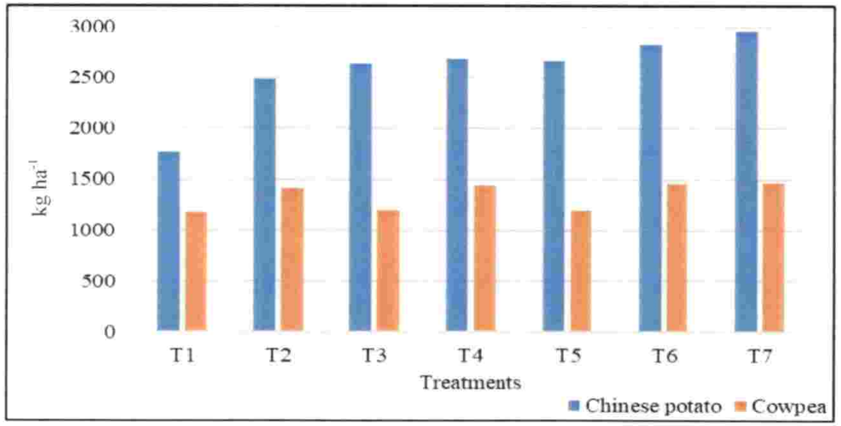

Fig. 39. Direct and residual effect of biochar on DMP (kg ha^{-1})

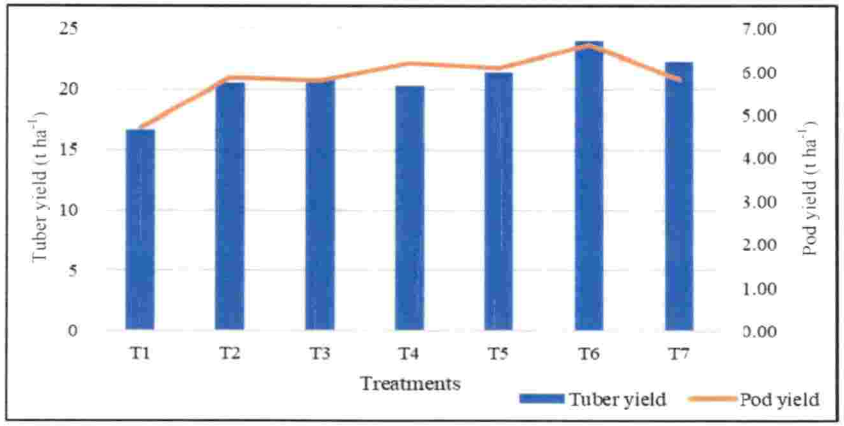

Fig. 40. Direct and residual effect of biochar on yield (t ha^{-1})

The very high porosity and surface area of biochar enable it to retain more water and nutrients in addition to providing an ideal habitat for the soil microorganisms which may the probable reason for crop yield improvement as reported by Lehmann and Rondon (2006) and Warnock *et al.* (2007).

The alkaline nature of biochar that lowered the exchangeable acidity thus raising the soil pH has provided a wide range of benefits in terms of soil quality especially by chemically improving nutrient availability and also by reducing the detrimental effect of elements like Al and Mn. The increase in pH brought about by biochar incorporation would also have resulted in the precipitation of exchangeable and soluble Fe and Al as their insoluble hydroxides thereby reducing its concentration in the soil solution. Application of biochar alone or together with fertilizers would have resulted in higher nutrient uptake and yield as reported from many investigations with biochar on crop yield (Cheng *et al.*, 2006; Verheijen *et al.*, 2010; Dainy, 2015).

The positive effect of soil test based POP and biochar on crop productivity obtained in the present experiment is due to the effect of biochar in the presence of N fertilizer on increasing N fertilizer use efficiency, which confirms with the findings of Chan *et al.* (2007) and Pan *et al.* (2009).

Results of the present investigation also describes the encouraging effect of biochar on soil CEC following which the ability to hold or bind the plant nutrient cations increases, thereby increasing the retention and reducing the leaching losses. With the application of biochar along with soil test based POP, the CEC increased from 3.72 to 4.95 cmol (+) kg^{-1} which explains the yield increase in the present experiment.

The significant and positive correlation between the growth components, yield and soil properties obtained in this present analysis reinforces the inference. Further confirmations were also arrived at from the stepwise regression analysis (Table 56) wherein, the growth components could be significantly predicted by soil properties. The data on path analysis to demarcate the direct and indirect effect on tuber yield presented in Table 57 showed the direct and moderate positive effect of plant height and average tuber girth on tuber yield in addition to the indirect effect through DMP, which was very high. The soil properties like organic carbon, MBC, Bray-P, NH_4OAc-K and Ca, and electrical conductivity directly influenced the tuber yield (Table 60). Results on post-harvest soil analysis showed the superior effect of biochar on soil properties which was identified as the key factor in yield improvement through path coefficients. This conclusively proves the positive effect of biochar on yield.

As could be expected the control plots which did not receive any manures or fertilizers had resulted in poor DMP, shorter plant stature, lower tuber girth and yield, which was the direct impact of reduced supply of nutrients to the growing plants besides poor physical and biological conditions.

For quantifying the residual effect of biochar, the growth components like plant height, number of pods per plant and DMP and pod yield were recorded. The data (Table 79) showed that the same treatment soil test based POP + biochar that faired in terms of direct effect proved good in bringing out the residual effect as well, as reflected from the plant height (39.74 cm), pod length (15.27 cm), number of pods per plant (14.17), DMP (1463.5 kg ha^{-1}) and pod yield (6.624 t ha^{-1}) (Fig. 38, 39 and 40).

Due to its resistance to decomposition in soil, one-time application of biochar can provide beneficial effects over several growing seasons in the field as given by Steiner *et al.* (2007) and Major *et al.* (2010). In the present study also, the usefulness of biochar was evidenced. Quite contrary to the organic manures, composts and synthetic fertilizers biochar does not call for continued application because of its strong carry over effect. Observations on the higher residual effect of biochar on crop growth and productivity has also been narrated by Lehmann (2003), Major *et al.* (2010), Islami *et al.* (2013), Elangovan (2014), Widowati *et al.* (2017), Sikder and Joardar (2018) and Sara *et al.* (2018).

5.4.3. Direct and residual effect of biochar on quality parameters

While the yield of crop is the ultimate goal of farming, the quality of economic part is also of equal importance in sustaining good health and for fetching higher prices. Therefore, addition of manures or any amendments should focus not

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only on yield improvement, but also in quality maintenance. There are ample evidences in the literature to show that incorporation of biochar could produce tastier and nutritive products which remain to be confirmed in the present investigation. Quality parameters assayed in the present study *viz.* carbohydrates and protein reflects the nutritive value of the product, whereas the crude fibre tells on the tenderness.

In tuber, the carbohydrate content estimated was highest in the treatment biochar 10 t ha^{-1} which was on par with soil test based POP + biochar. Protein content on the other hand was highest in the treatments soil test based POP (1.742 %) and soil test based POP + biochar (1.682 %). However, the protein content observed in the control plots was only 1.356 per cent. In respect of crude fibre, the treatment effect was comparable (Fig. 41).

The advantage of biochar on increasing protein content and decreasing crude fibre content are visible from the data pertaining to vegetable cowpea given in Table 87. The results on biochar effect on quality attributes tallies fully with the test crops Chinese potato and vegetable cowpea (Fig. 42). The beneficial role of biochar on crop quality was further confirmed through simple correlation and stepwise regression analysis.

5.4.4. Direct and residual effect of biochar on nutrient content and uptake by crop

Nutrient content in the economic part of any plant is considered to be an important quality criterion, since it ultimately determines the quantity of nutrients consumed by human beings. With the recent awareness with respect to nutritional security, this aspect gains greater significance. In this present study too, the nutrient content was estimated in the plant parts of Chinese potato and vegetable cowpea with an intention to study the effect of biochar on the mineral profile of crop. Making use of the data on nutrient content, uptake of nutrients by crop was also computed.

Nutrient uptake depends on the concentration of respective nutrient in different plant parts and DMP. While at the initial stages of crop growth the DMP is controlled by the soil nutrient supply, at later stages as the crop nears its maturity the

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nutrient supply from soil may not have greater impact. For that reason, at the earlier stages of crop growth the concentration of nutrients will be higher as the nutrient supply exceeds the rate of DMP while at later stages the rate of DMP exceeds the rate of nutrient supply. The concentration of nutrient gets reduced following the dilution effect. Eventually the nutrient uptake is a function of the supply of corresponding nutrients, whereas partitioning of nutrient supply between the plant parts and economic product is a function of genetic makeup of the plant as well as nutrient supply from the soil. While the soils capacity to supply nutrient could be predicted by the chemical analysis of soils, the ultimate availability is adjudicated by the crop in terms of its uptake values. That being the case, it is quite essential to evaluate the fruitfulness of different treatments imposed not only by their effect on nutrient availability as estimated by analysis but also by computing nutrient uptake. The present study had showed beyond doubt that applied treatments positively affected the nutrient content and uptake.

The content of N in haulm was found to be higher with the application of biochar 10 t ha^{-1}, whereas the tuber N content was higher with the treatments soil test based POP and soil test based POP + biochar (Fig. 43). With respect to the residual effect of applied treatments, biochar applied at higher doses (7.5 and 10 t ha^{-1}) influenced the content of N in both shoot and pod by recording higher values (Fig. 45). Soil test based POP + biochar application showed its superior effect by registering higher total N uptake in both the experiments. However, it was on par with biochar 7.5 t ha^{-1} and soil test based POP in the second experiment (Fig. 47, 49).

Phosphorus content of haulm was significantly higher in the treatments biochar 10 t ha^{-1}, whereas in case of tuber higher values was shared by biochar 10 t ha^{-1} and soil test based POP (Fig. 43). The graded doses of biochar application (5, 7.5 and 10 t ha^{-1}) and FYM 10 t ha^{-1} had a comparable residual effect on the P content (Fig. 45). Regarding the total uptake, direct effect was exhibited more by biochar 10 t ha^{-1} and soil test based POP + biochar. Residual effect was also high in the treatment soil test based POP + biochar which was comparable with biochar 7.5 t ha^{-1} and FYM 10 t ha^{-1} (Fig. 47 and 49).

Potassium content in tuber did not vary much due to the applied treatments, but its concentration in haulm was higher with soil test based POP + biochar application. Regarding the residual effect, the graded levels of biochar had significant effect (Fig. 45). Considering the total K uptake, integrated application of NPK and biochar recorded higher values, thereby registering its high direct and residual effect on crop plants (Fig. 47 and 49).

Calcium content of haulm was significantly higher with biochar 10 t ha^{-1}. Application of biochar at the rate of 7.5 and 10 t ha^{-1}, soil test based POP registered higher total Ca uptake in case of Chinese potato (Fig. 47) whereas in vegetable cowpea the residual effect of treatments biochar 5 and 7.5 t ha^{-1} and soil test based POP showed greater effect on Ca content and uptake (Fig. 45 and 49).

Regarding the direct effect of treatments on Mg content and uptake, soil test based POP, soil test based POP + biochar, biochar 10 t ha^{-1} and FYM 10 t ha^{-1} showed their superiority (Fig. 43 and 47). On considering the residual effect, combined application of biochar and NPK, sole application of FYM 10 t ha^{-1} alone maintained its supremacy (Fig. 45 and 49).

Content of S in haulm, tuber and its total uptake was found to be largely influenced by the graded levels of biochar application, soil test based POP and soil test based POP + biochar (Fig. 43 and 47). The residual effect of different treatments on S content and uptake was only comparable (Fig. 45 and 49).

The content of Fe and Mn in haulm was found to increase with the application of treatments. The higher value was recorded by soil test based POP in respect of Fe and soil test based POP and soil test based POP + biochar in case of Mn. As regards the tuber, graded levels of biochar application recorded higher Fe values, whereas biochar 10 t ha^{-1} and its integration with NPK recorded higher Mn. On evaluating the total Fe and Mn uptake, the treatments soil test based POP and soil test based POP + biochar showed superiority in registering higher values (Fig 44 and 48).

The residual effect of different treatments on content and uptake of Fe and Mn differed from the direct. Higher values with respect to the content of Fe and Mn in shoot was observed in control plots. As regards the tuber, Fe content was found to be the lowest in the treatments soil test based POP + biochar and soil test based POP and the Mn content was lower in biochar 10 t ha^{-1} and soil test based POP + biochar. Considering the total uptake, the higher values was associated with control, and the lowest with biochar 5 and 10 t ha^{-1} for Fe and Mn, respectively. The graded levels of biochar had significant effect on reducing the Fe and Mn content in cowpea pods (Fig. 46 and 50).

Content of Zn in haulm was increased by the application of biochar 10 t ha^{-1}, whereas the Zn content of tuber was increased by soil test based POP, soil test based POP + biochar application (Fig. 44). The treatments biochar 10 t ha^{-1}, soil test based POP and soil test based POP + biochar had pronounced effect on the total Zn uptake and the effect was comparable within them (Fig. 48). On evaluating the residual effect, the treatment biochar 10 t ha^{-1} was found superior in registering higher Zn content and its integration with NPK showed predominance in Zn uptake (Fig. 46 and 50).

Regarding Cu content of haulm and tuber, the treatments biochar 10, 7.5 and 5 t ha^{-1} and the treatment soil test based POP recorded the higher values, respectively (Fig. 44). While considering the direct effect of treatments on total Cu uptake, it was seen that soil test based POP and soil test based POP + biochar were superior, whereas in case of residual effect, the treatments biochar 5 and 7.5 t ha^{-1} and soil test based POP were superior (Fig. 48 and 50).

With respect to B, the content in haulm was higher in control, FYM 10 t ha^{-1} and biochar 5 t ha^{-1}, whereas in case of tuber the content was higher with soil test based POP + biochar, soil test based POP and biochar 10 t ha^{-1} (Fig. 44). On evaluating the residual effect, the treatments biochar 10, 7.5 and 5 t ha^{-1} and FYM 10 t ha^{-1} showed predominance. Residual effect on total B uptake was only comparable (Fig. 50).

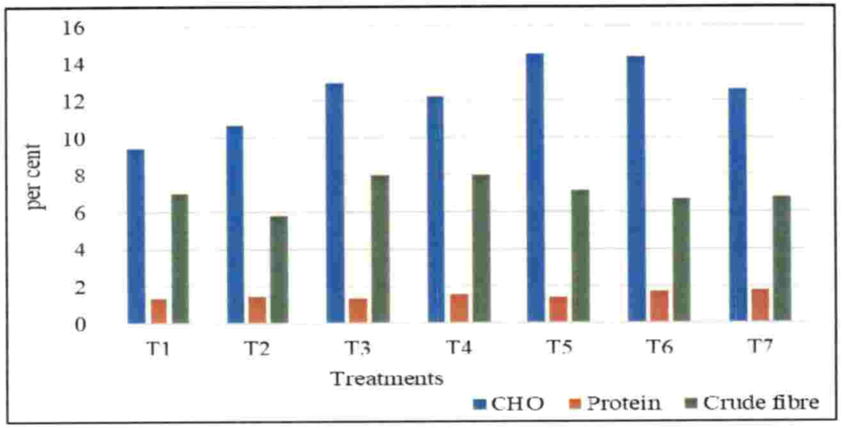

Fig. 41. Effect of biochar application on quality attributes (%) of Chinese potato tuber

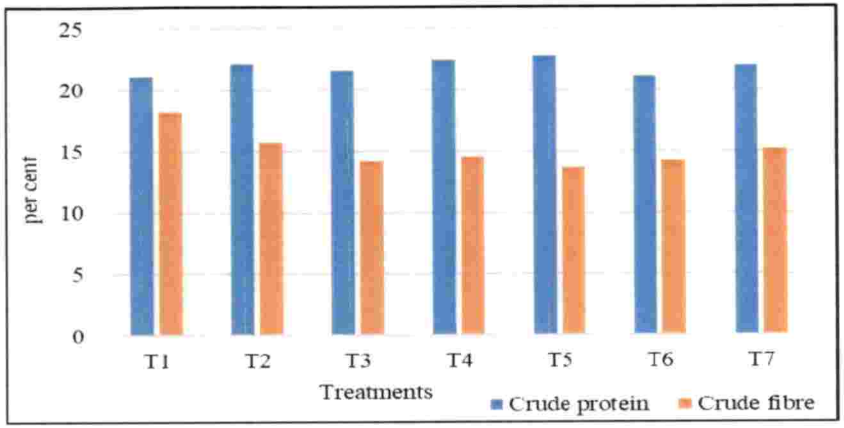

Fig. 42. Effect of biochar application on quality attributes (%) of cowpea pod

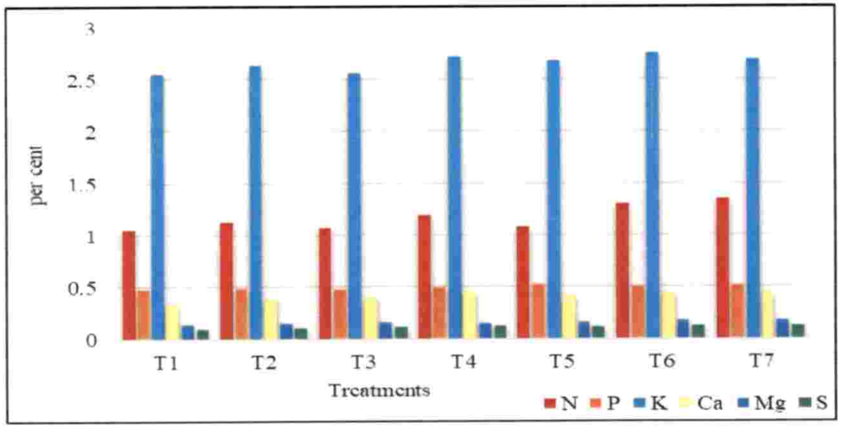

Fig. 43. Direct effect of biochar on macronutrient content (%) in Chinese potato tuber

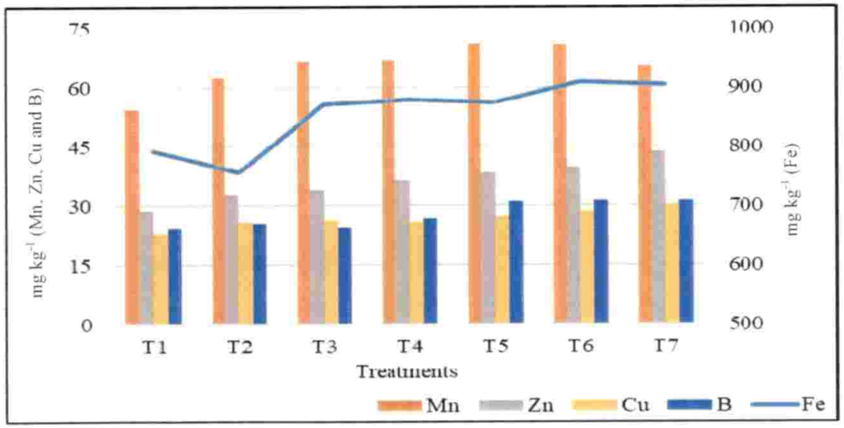

Fig. 44. Direct effect of biochar on micronutrient content in Chinese potato tuber (mg kg^{-1})

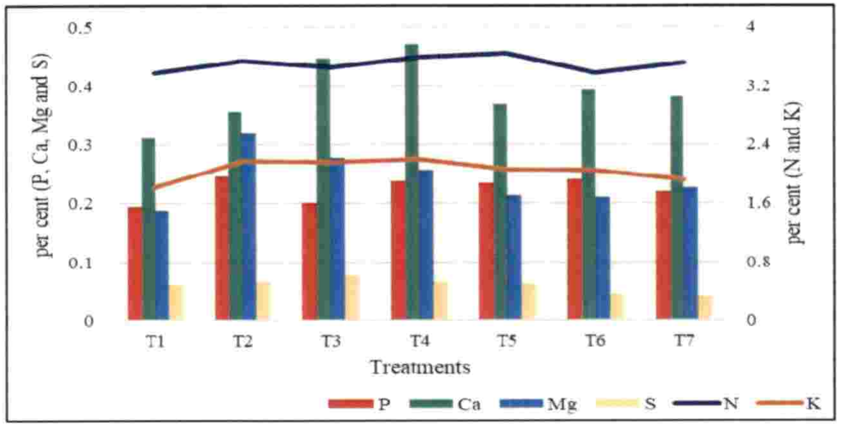

Fig. 45. Residual effect of biochar on macronutrient content (%) in cowpea pod

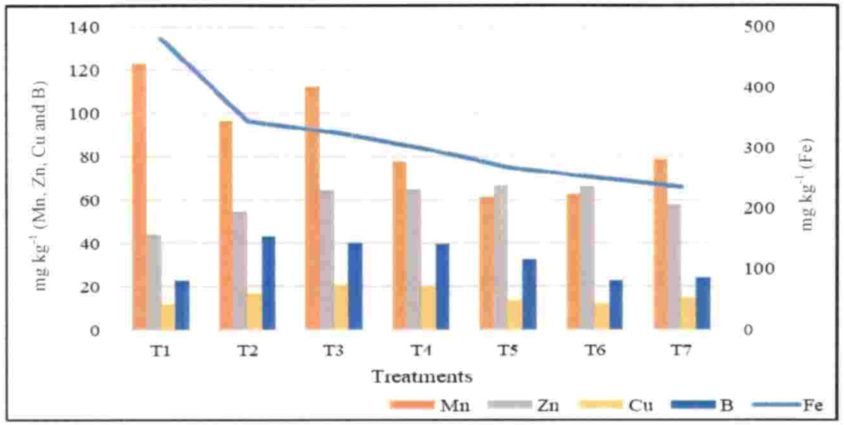

Fig. 46. Residual effect of biochar on micronutrient content in cowpea pod (mg kg^{-1})

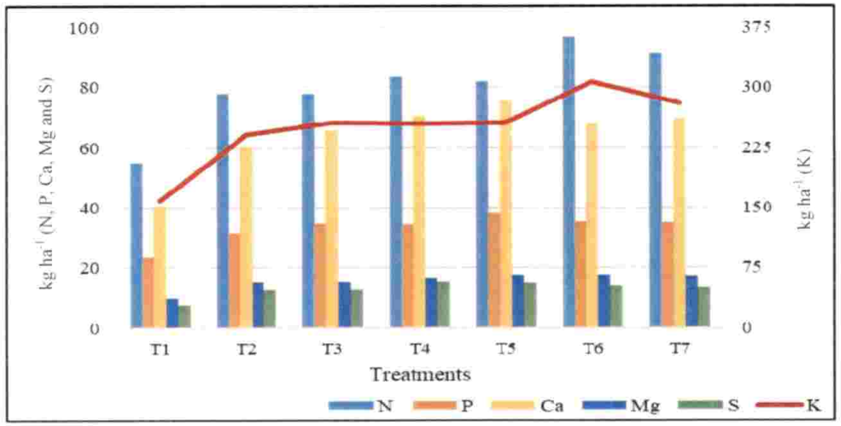

Fig. 47. Direct effect of biochar on total uptake of macronutrients (kg ha^{-1}) by Chinese potato

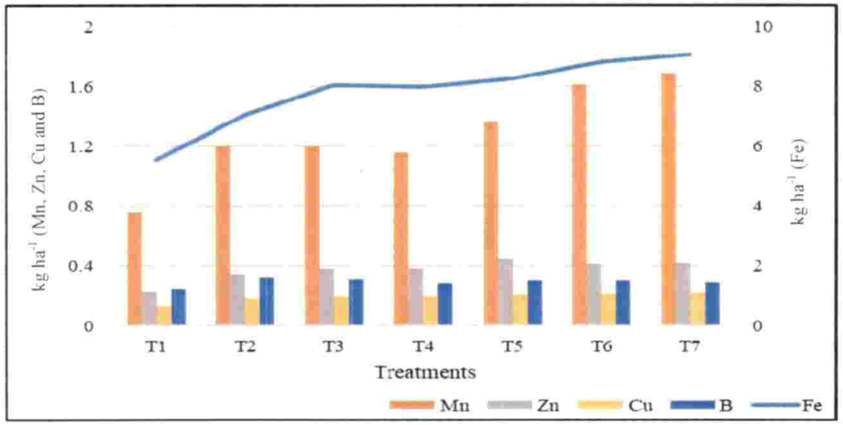

Fig. 48. Direct effect of biochar on total uptake of micronutrients (kg ha^{-1}) by Chinese potato

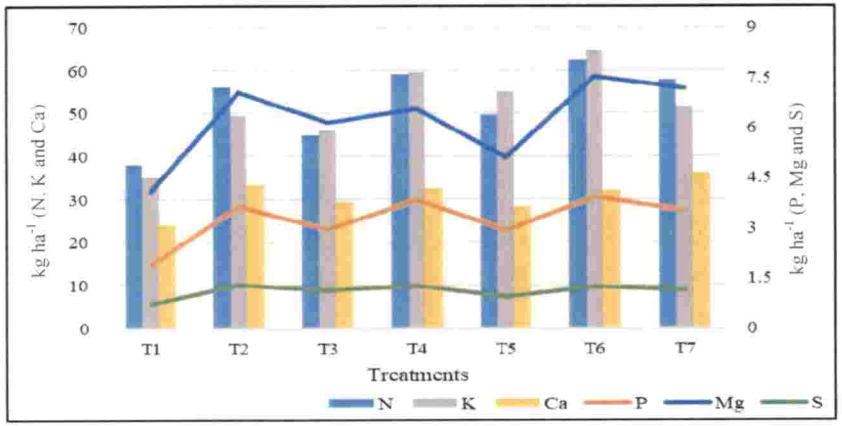

Fig. 49. Residual effect of biochar on total uptake of macronutrients (kg ha^{-1}) by cowpea

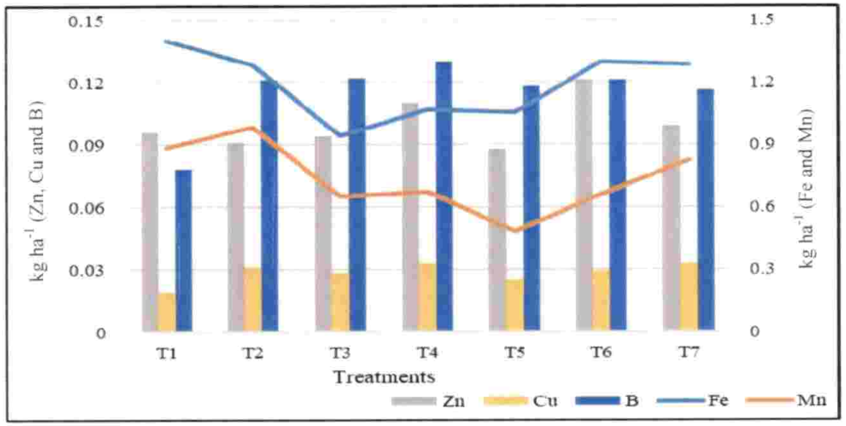

Fig. 50. Residual effect of biochar on total uptake of micronutrients (kg ha^{-1}) by cowpea

From the foregoing interpretations on results, it is evident that the nutrient content and uptake of plant increased due to the addition of different treatments. Such a trend could be related to the increase in availability of these nutrients in soil ant their higher uptake and their translocation to the different plant parts efficiently. Though the growth of plant in itself and the resultant biomass is sufficient enough to give higher uptake of nutrients, the further difference noticed in nutrient uptake is the direct impact of treatment imposed. The results and the discussions on post-harvest soil analysis sturdily denotes the promising effect of biochar either alone or in combination with inorganic fertilizers on enhancing nutrient availability either directly by nutrient addition or indirectly through modifying the chemistry of soil. This clearly reassures the statement "An increase in the soil nutrient availability, increases the content of respective nutrient in plant". In the present study also, the changes in nutrient uptake could be related to the increase in nutrient content and DMP, brought about by the increased availability of corresponding nutrients, following biochar application.

Water, the universal solvent that controls and governs the solubility and uptake of all nutrients in the soil system. This statement holds good in the present work also, where the biochar was observed to have promotional effect on soil water content and in turn an increased nutrient uptake. Furthermore, the increased assimilation of the primary nutrient N will also enhance the uptake of other nutrients mainly through the promotion of root growth (Santonoceto *et al.*, 2002). Direct addition of nutrients by biochar is also of greater importance especially for major nutrients (P, K, Ca, Mg) and micronutrients. Yet another reason for increased nutrient content and uptake suggested by many researchers is the favourable effect on soil pH, especially in an acidic soil following biochar addition which decreases Al activity, bettering root growth and in turn a higher nutrient uptake. Nigussie *et al.* (2012) highlighted the presence of essential plant nutrients, its high surface area, porous nature and the capacity of biochar to act as a medium for soil microorganisms as the prime reasons for the enhancement in soil properties, leading to increased nutrient content and uptake in plants whenever supplied with biochar. Increase in micronutrient content and uptake might be due to the presence of chelated micronutrients in the applied biochar, as opined by Major (2009).

Significant and positive correlation between available nutrient status of post-harvest soil and nutrient content at harvest further add support on to the conclusions drawn. For instance, the content of P in tuber was positively related with CEC, Bray-P, NH_4OAc-Ca and Mg and HCl-Mn (Table 65) and the content of P in pod was positively correlated with pH, organic carbon, CEC, dehydrogenase activity, Bray-P, NH_4OAc-Mg, HCl-Zn and hot water soluble boron (Table 90), which clearly indicated the beneficial role of soil properties, particularly the soil available P status. Similar correlations were also established between soil properties and the content of nutrients like N, K, Ca, Mg, S and micronutrients. Further confirmations were also arrived at from the stepwise regression analysis (Table 66 and 91), wherein the nutrient content was significantly predicted by soil properties.

Similar to that of the nutrient content in plant, the nutrient uptake was also found to be significantly influenced by soil properties, which is fully supported by the simple correlation and stepwise regression analysis. For instance, the total N uptake by Chinese potato correlated with the soil properties *viz.* pH, EC, organic carbon, CEC, MBC, dehydrogenase activity, $KMnO_4$-N, Bray-P, NH_4OAc- K, Ca and Mg, $CaCl_2$-S and HCl-Zn (Table 67), which clearly proved the role of soil properties, particularly organic carbon, MBC, dehydrogenase activity and $KMnO_4$-N on the uptake of N by plants. Significant contribution of soil properties on uptake of nutrients noticed in the stepwise regression analysis further supports the results (Table 68 and 93). Similar observations of higher nutrient content and uptake due to biochar addition either alone or in combination with NPK has also been reported by Glaser *et al.* (2002), Lehmann *et al.* (2003), Lehmann and Rondon (2006), Liang *et al.* (2006), Chan *et al.* (2007), Novak *et al.* (2009), Hossain *et al.* (2010), vanZwieten *et al.* (2010), Uzoma *et al.* (2011), Rajkovich *et al.* (2012), Elangovan (2014), Akshatha (2015) and Dainy (2015), Walter and Rao (2015), Abbas *et al.* (2017) and Hamdani *et al.* (2017).

Summary

6. SUMMARY

The present investigation titled "Aggrading lateritic soils (Ultisol) using biochar" was carried out in three phases *viz.* production and characterization of biochar, an incubation experiment at Department of Soil Science and Agricultural Chemistry, College of Horticulture, Vellanikkara and two field experiments at Agricultural Research Station, Mannuthy, during the period 2016-2018. The incubation experiment was conducted for 15 months simulating the crop duration, to study the carbon and nitrogen dynamics in soil over time and also to assess the maximum water holding capacity. The soil samples were drawn at three months interval and subjected to analysis of various carbon and nitrogen fractions. Two field experiments were carried out successively under natural environment in Fine loamy kaolinitic, isohyperthermic soil (Typic plinthustults), wherein the first one was with Chinese potato as a test crop to study the direct effect of biochar and the second one with cowpea as the test crop to study the residual effect of biochar that was applied to the first crop. Soil and plant samples were collected at the harvest stage to study the effect of treatments on soil properties, growth, yield and quality of crop and also on its nutrient uptake. The salient research findings are summarized experiment wise as follows.

Production and characterization of biochar

- Biochar was produced from slow pyrolysis of coconut shell and husk in 1:1 ratio, using the kiln exclusively designed for this purpose. On an average 22 kg of biochar could be produced from 100 kg raw material
- Bulk density and particle density of the biochar were 0.128 and 0.833 Mg m^{-3} each. Biochar was highly porous (84.63 %) with MWHC of 307.3 per cent. Ash content constituted 11.33 per cent
- Biochar was alkaline in nature (10.01) with an EC of 3.42 dS m^{-1}. The CEC was 15.78 cmol (+) kg^{-1} with K and Ca as the dominant cations
- Content of C was very high (64.14 %) resulting in a C: N ratio of 113:1

- The content of major nutrients in biochar was 0.567 per cent N, 0.982 per cent P and 4.175 per cent K. In addition, it also contained significant amount of secondary nutrients *viz.* 1.19, 0.456 and 0.244 per cent Ca, Mg and S, respectively

- Basicity and acidity of biochar were 2.02 and 0.08 mmol g^{-1}, respectively

- Scanning electron microscope image revealed the external morphology of biochar as follows

  - Highly disordered and complex morphology with longitudinal channels and pores

  - Pores of different shapes and size *viz.* ellipsoidal, hollow and scattered over the surface

  - Irregular flakes, irregular surface with polygonal shards and layered sheets are the other surface features

- The internal morphology of biochar imaged using TEM showed the presence of localized crystalline graphite like structure, an indicative of C, the most dominant atom of the experimental biochar

- FT-IR and Raman spectrum of biochar clearly showed the presence of more number of aromatic C groups, indicating the recalcitrant nature of biochar C

- Additionally, both FT-IR and Raman spectrum clearly explained that the produced biochar contained higher amount of C, H, O and traces of N, S, P and Si on its surface

- Furthermore, the results suggested that the biochar can be used as a soil amendment for improving the properties of lateritic soils, especially with reference to pH, CEC in addition to acting as a potential adsorbent

Incubation experiment

- With the advancement in incubation period, the total carbon content decreased initially and then slightly increased upto 6 months of incubation, followed by a further decrease

- Among the different treatments tried, soil test based POP + biochar registered the significantly higher total C value (2.439 %), followed by biochar at the rate of 10 t ha^{-1} (2.331 %), 7.5 t ha^{-1} (2.247 %) and 5 t ha^{-1} (2.180 %)
- As regards the organic carbon content, soil test based POP + biochar recorded the highest values throughout the incubation period, whereas the control recorded the lowest
- With the advancement of incubation period, there was a decline in the organic carbon content
- Rate of decrease in organic carbon was highest in soil test based POP (4.177 mg kg^{-1} day^{-1}). With an increase in the biochar levels, sharp reduction was noticed in the rate of decrease. Applying biochar together with inorganic fertilizer sources further aggravated the reduction
- Irrespective of incubation period, WSC content ranged from 92.61 to 111.5 mg kg^{-1}, with the treatment FYM 10 t ha^{-1} recording the highest
- Much alike the organic carbon, the WSC also increased upto 6 months of incubation and decreased thereafter
- In case of HWSC also the treatment FYM 10 t ha^{-1} registered the highest values, irrespective of incubation period and its concentration decreased with advancement of incubation in all treatments
- Content of POXC showed a significant decrease with advancement of incubation, where it reduced to 890.2 from initial value of 1549.8 mg kg^{-1}.
- The POXC content registered was comparable in respect of soil test based POP, soil test based POP + biochar and biochar 10 t ha^{-1}
- An increase in biochar level brought about increase in the POXC content also
- The rate of decrease in POXC was maximum in control, whereas the minimum rate of decrease of 0.993 mg kg^{-1} day^{-1} was associated with soil test based POP treatment. Including NPK fertilizer along with biochar added on to the rate of reduction in POXC

- During the incubation, MBC content got increased and reached a maximum at 6 months and declined thereafter. However, the values were always higher than the initial day of incubation

- Irrespective of stages, the MBC was found to be the highest in the soil applied with soil test based POP (136.2 mg kg^{-1}) and biochar at 10 t ha^{-1} (133.2 mg kg^{-1}), which were on par

- With an increase in the levels of biochar, the MBC content also increased

- As against the control, NH_4-N fraction was higher in the treatments soil test based POP + biochar and soil test based POP, which were on par

- With the progression of incubation, NH_4-N declined steadily at 3 MAI, then increased upto 9 months of incubation after which it decreased till the incubation ended

- Quite contrary to NH_4-N, incubation had a significant effect in increasing NO_3-N content from 224.3 mg kg^{-1} (O MAI) to 435.2 mg kg^{-1} (12 MAI). The treatment effect was similar as that of NH_4-N

- The rate of NO_3 release was maximum with soil test based POP (0.702 mg kg^{-1} day^{-1}), followed by soil test based POP + biochar (0.595 mg kg^{-1} day^{-1}) and was minimal in control

- The rate of release of NO_3-N (0.446 mg kg^{-1} day^{-1}) in the biochar (10 t ha^{-1}) alone treatment got enhanced to 0.595 mg kg^{-1} day^{-1}, when soil test based POP was combined with biochar application

- The treatments soil test based POP and soil test based POP + biochar were comparable in terms of THyN in registering higher values of 1499 and 1477 mg kg^{-1}, respectively

- Advancement in incubation had a favourable effect on THyN as reflected form the increase noticed upto 6 months of incubation, where the maximum value was recorded. A progressive decrease was noticed after 6 months and reached at 1215 mg kg^{-1} towards the end

- The AAN fraction was found to be the highest in the treatment soil test based POP (513.8 mg kg^{-1}), followed by soil test based POP + biochar (508.2 mg kg^{-1}), which were on par

- With an advancement in incubation, AAN fraction increased upto 12 months of incubation and declined thereafter. Though the content declined during 15 months, the reduction was not as much compared to initial value

- Total N was lowest in the soil alone treatment at all stages of incubation whereas the treatments soil test based POP, soil test based POP + biochar, biochar 5 t ha^{-1} and FYM 10 t ha^{-1} were highest in terms of total N

- Significantly highest $KMnO_4$-N value was associated with soil test based POP, followed by soil test based POP + biochar.

- With an increase in biochar levels, $KMnO_4$-N also increased though only marginally

- Irrespective of sampling periods, the treatment soil test based POP and soil test based POP + biochar application yielded higher values for $KMnO_4$-N

- The rate of $KMnO_4$-N release was maximum in soil test based POP + biochar, followed by soil test based POP. Application of biochar alone had a reduced effect on the rate of release as against its application along with NPK

- The carbon fractions *viz.* MBC and total carbon maintained positive correlation with $KMnO_4$-N, whereas WSC, HWSC and POXC had negative correlation. Among the N fractions, NO_3-N and AAN alone had a positive relationship with $KMnO_4$-N

- The direct effect of MBC and total carbon on $KMnO_4$-N status was very high and positive, whereas the direct effect of WSC was very high and negative

- The direct effect of NO_3-N on $KMnO_4$-N was very high and positive. The direct contribution of AAN was low, whereas its indirect effect through NO_3-N was positive and very high

- Application of biochar 10 t ha^{-1} recorded the highest MWHC of 36.02 per cent, followed by soil test based POP + biochar (35.75 %) as against 33.31 per cent recorded in the control
- At all stages of incubation, the superiority of biochar 10 t ha^{-1} and soil test based POP + biochar was prominent
- With increase in biochar level, MWHC also showed an increase

Field experiments

- The pH of post-harvest soil increased to 5.95 from the initial value of 5.24 in the treatment biochar 10 t ha^{-1} and the same treatment maintained superiority after both the test crops
- As regards the EC, soil test based POP + biochar registered the highest value of 0.084 dS m^{-1}, followed by soil test based POP alone
- Organic carbon content increased from 1.55 per cent in the beginning of experiment to 1.778 per cent after the first crop and to 1.767 per cent after the second crop. In both experiments, application of biochar 10 t ha^{-1} either alone or in combination with soil test based POP showed a superior effect by registering significantly higher values
- Increase in levels of biochar on increasing the content of organic carbon was noticed in both experiments
- Exchangeable acidity was highest for the treatment soil test based POP (0.093 meq $100g^{-1}$) followed by the control, whereas it was lowest in case of biochar 10 t ha^{-1}, both after Chinese potato and vegetable cowpea. There was reduction in exchangeable acidity with an increase in the biochar application rate though marginal
- With respect to the $KMnO_4$-N content, soil test based POP + biochar recorded higher values, but the effect was on par with biochar 5 t ha^{-1} after the first season and with biochar 5 t ha^{-1} and soil test based POP after succeeding crop

- Bray-P content of soil increased in all the treatments in comparison with the initial value (27.08 kg ha^{-1}). In the post-harvest soil of main crop, soil test based POP + biochar registered higher value however it was on par with soil test based POP and FYM 10 t ha^{-1}. In the succeeding crop also the same treatment showed superiority in registering higher values

- NH_4OAc extractable K, Ca and Mg increased during the experimental period. The K content was higher with the application of biochar 10 t ha^{-1}, whereas the Ca and Mg content was more with soil test based POP + biochar

- Levels of biochar had a significant effect on increasing K content

- Promotional effect of soil test based POP and soil test based POP + biochar on $CaCl_2$ extractable S was observed. However, biochar alone did not have any significance on increasing $CaCl_2$-S status

- The effect of different treatments on HCl-Fe was only comparable

- In terms of HCl-Mn, it was found to be higher in the treatment biochar 10 t ha^{-1}, which was comparable with all other treatments. In the succeeding crop, significantly lowest amount of HCl-Mn was recorded by the treatment biochar 10 t ha^{-1}, which in fact was the one that showed highest HCl-Mn content during the main crop

- During the main crop, HCl extractable Zn was higher in the treatment soil test based POP + biochar, which was on par with FYM 10 t ha^{-1}. There was only marginal effect after the second crop

- With an increase in biochar levels, the HCl-Zn increase was marginal

- The HCl-Cu content was highest in the treatment biochar 10 t ha^{-1} during the main crop and biochar 7.5 t ha^{-1} after the next crop, followed by rest of the treatments which were comparable with each other

- HCl extractable Fe, Mn and Cu showed an increasing trend throughout the experiment, whereas the Zn content increased during the first crop and decreased thereafter

- As regards the boron content, the treatments biochar 10 and 7.5 t ha^{-1} registered higher values during the main crop, whereas in the ensuing crop biochar 7.5 t ha^{-1} and soil test based POP + biochar recorded higher values

- Application of soil test based POP + biochar and biochar 10 t ha^{-1} were found to increase the dehydrogenase activity of post-harvest soil during the first experiment. However, in the post-harvest soil of succeeding crop, the treatment soil test based POP + biochar showed superiority by registering higher dehydrogenase activity

- With an increase in biochar application rate, the dehydrogenase activity increased, though it was only marginal

- Dehydrogenase activity got enhanced to 163.6 μg TPF g^{-1} soil 24hr^{-1} than the sole application of biochar 10 t ha^{-1} (93.12) and soil test based POP (116.1)

- The treatments that contained high quantity of biochar *viz.* soil test based POP + biochar, biochar 10 t ha^{-1} and biochar 7.5 t ha^{-1} registered higher CEC values. Increasing levels of biochar also increased the CEC

- The treatments biochar 10 t ha^{-1} and soil test based POP + biochar recorded higher MWHC values in the field experiment also much alike incubation experiment

- The treatments that contained biochar in it and the treatment FYM 10 t ha^{-1} had a comparable effect on fulvic acid content. In the case of humic acid fraction, application of graded levels of biochar *viz.* 7.5 and 10 t ha^{-1} and its integration with soil test based POP increased its content

- The treatment soil test based POP recorded the highest values for plant height (72.66 cm), average tuber girth (3.37 cm) and DMP (2959.3 kg ha^{-1}) which was comparable with soil test based POP + biochar

- In terms of tuber yield, the treatment soil test based POP + biochar registered the highest value of 24.04 t ha^{-1}

- The same treatment soil test based POP + biochar that faired in terms of direct effect proved good in bringing out the residual effect as well, as reflected from the plant height, pod length, number of pods per plant, DMP and pod yield

- Path analysis showed the direct and moderate positive effect of plant height and average tuber girth on tuber yield in addition to the indirect effect through DMP, which was very high
- The soil properties like organic carbon, MBC, Bray-P, NH_4OAc-K and Ca, and electrical conductivity directly influenced the tuber yield
- Results on post-harvest soil analysis showed the superior effect of biochar on soil properties which were identified as the key factor in yield improvement
- With respect to the quality attributes, the treatments biochar 10 t ha^{-1} and soil test based POP + biochar recorded higher CHO content. Protein content was highest in the treatments soil test based POP and soil test based POP + biochar
- The advantage of biochar on increasing protein content and decreasing crude fibre content were visible in the succeeding crop, thus establishing its high residual effect
- The N content of haulm was found to be higher with the application of biochar 10 t ha^{-1}, whereas the tuber N content was higher with the treatments soil test based POP and soil test based POP + biochar
- With respect to the residual effect, biochar applied at higher doses (7.5 and 10 t ha^{-1}) influenced the content of N in both shoot and pod. Soil test based POP + biochar application showed its superior effect by registering higher total N uptake in both the experiments
- Phosphorus content of haulm was significantly higher in the treatments biochar 10 t ha^{-1}, whereas in case of tuber higher values was shared by biochar 10 t ha^{-1} and soil test based POP. The graded doses of biochar application and FYM 10 t ha^{-1} had a comparable residual effect on the P content

- Regarding the total P uptake, direct effect was exhibited more by biochar 10 t ha^{-1} and soil test based POP + biochar. Residual effect was also high in the treatment soil test based POP + biochar which was comparable with biochar 7.5 t ha^{-1} and FYM 10 t ha^{-1}

- Potassium content in tuber did not vary much due to the applied treatments, but its concentration in haulm was higher with soil test based POP + biochar application. Regarding the residual effect, the graded levels of biochar had significant effect. Integrated application of NPK and biochar recorded higher K uptake, thus registering its high direct and residual effect on crop plants

- Calcium content of haulm was significantly higher with biochar 10 t ha^{-1}. Application of biochar at the rate of 7.5 and 10 t ha^{-1}, soil test based POP registered higher total Ca uptake in case of Chinese potato. However, in vegetable cowpea the residual effect of treatments biochar 5 and 7.5 t ha^{-1} and soil test based POP showed greater effect on Ca content and uptake

- Soil test based POP, soil test based POP + biochar, biochar 10 t ha^{-1} and FYM 10 t ha^{-1} showed their superior direct effect on Mg content and uptake. As regards the residual effect, combined application of biochar and NPK, sole application of FYM 10 t ha^{-1} alone maintained its supremacy

- Content of S in haulm, tuber and its total uptake was found to be largely influenced by the graded levels of biochar application, soil test based POP and soil test based POP + biochar

- With respect to the content of Fe and Mn in haulm, the higher value was recorded by soil test based POP in respect of Fe and soil test based POP and soil test based POP + biochar in case of Mn. As regards the tuber, graded levels of biochar application recorded higher Fe values, whereas biochar 10 t ha^{-1} and its integration with NPK recorded higher Mn

- Regarding the total Fe and Mn uptake, the treatments soil test based POP and soil test based POP + biochar showed superiority

- The residual effect of different treatments on content and uptake of Fe and Mn differed from the direct. The graded levels of biochar had significant effect on reducing the Fe and Mn content in cowpea pods

- Content of Zn in haulm was increased by the application of biochar 10 t ha^{-1}, whereas the Zn content of tuber was increased by soil test based POP and soil test based POP + biochar application. The treatments biochar 10 t ha^{-1}, soil test based POP and soil test based POP + biochar had pronounced effect on the total Zn uptake

- On evaluating the residual effect, the treatment biochar 10 t ha^{-1} was found superior in registering higher Zn content and its integration with NPK showed predominance in Zn uptake

- As regards the Cu content of haulm and tuber, the treatments biochar 10, 7.5 and 5 t ha^{-1} and the treatment soil test based POP recorded the higher values, respectively. While considering the direct effect of treatments on total Cu uptake, it was seen that soil test based POP and soil test based POP + biochar were superior, whereas in case of residual effect, the treatments biochar 5 and 7.5 t ha^{-1} and soil test based POP were superior

- With respect to B, the content in haulm was higher in control, FYM 10 t ha^{-1} and biochar 5 t ha^{-1}, whereas in case of tuber the content was higher with soil test based POP + biochar, soil test based POP and biochar 10 t ha^{-1}. On evaluating the residual effect, the treatments biochar 10, 7.5 and 5 t ha^{-1} and FYM 10 t ha^{-1} showed predominance. Residual effect on total B uptake was only comparable

- The step wise regression analysis and path analysis revealed that, the soil properties could significantly explain the variation in plant growth, yield, nutrient content and uptake which were the net effect of biochar and fertilizer addition

Combined application of biochar with soil test based POP has proved it as a potential tool for improving soil properties, higher plant nutrition, crop yield and quality in the acidic lateritic soil. Unlike the commonly used organic manures that get degraded and decomposed rapidly under tropical conditions, biochar with its strong residual effect and recalcitrant nature could prolong the sequestration of carbon as reflected from the higher yield of vegetable cowpea grown after Chinese potato. The yield increased to an extent of 14 per cent over soil test based POP.

Easiness of producing biochar from any biomass at low cost or zero cost and its advantages over other prevailing organic manures whose timely unavailability and high cost need to apply on regular basis makes biochar a kind of modifier to improve acidic soil. However, concerted long term and large scale field experiments are required to assess the benefit over time and to quantify the amount of recalcitrant carbon supplied and sequestered.

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Abstract

AGGRADING LATERITIC SOILS (ULTISOL) USING BIOCHAR

by

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ABSTRACT OF THE THESIS

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ABSTRACT

The present investigation was undertaken at College of Horticulture, Vellanikkara and Agricultural Research Station, Mannuthy during 2016-2018. The study consisted of production and characterization of biochar from coconut based materials, an incubation experiment, and two field experiments. The incubation experiment was conducted for 15 months to study the dynamics of C and N in soil over time and the soil samples were analyzed for C and N fractions at three months' interval. Two field experiments were carried out sequentially, wherein Chinese potato was raised to study the direct effect of biochar and vegetable cowpea was the test crop to study the residual effect of biochar applied to the first crop. Three levels of biochar (5, 7.5, 10 t ha^{-1}), FYM 10 t ha^{-1}, soil test based POP + biochar 10 t ha^{-1} and soil test based POP were the treatments, for both incubation and field experiments. Soil test based POP consisted of NPK and FYM 10 t ha^{-1}. Control plots without the addition of biochar/fertilizers were also maintained.

Recovery of biochar from coconut husk and shell (1:1) on pyrolysis was 22 per cent. The produced biochar had an alkaline pH (10.01), high EC (3.42 dS m^{-1}), C (64.14 %), CEC (15.78 cmol (+) kg^{-1}), and C: N ratio (113:1). Total N, P, K, Ca, Mg and S contents were 0.567, 0.982, 4.175, 1.19, 0.456 and 0.244 per cent, respectively. Regarding physical properties, biochar had low bulk density (0.128 Mg m^{-3}), very high porosity (84.63 %) and WHC (307.3 %). Basicity and acidity of biochar were 2.02 and 0.08 mmol g^{-1}, respectively. The surface morphology and chemistry studied using SEM, TEM, FT-IR and Raman spectroscopy revealed the porous, aromatic and recalcitrant nature of biochar and the presence of functional groups mainly carboxyl, hydroxyl and carbonyl.

Results of incubation experiment revealed that the content of organic carbon (OC), water soluble carbon (WSC) and microbial biomass carbon (MBC) increased up to 6 months of incubation and decreased thereafter. In the case of permanganate oxidizable carbon (POXC) and hot water soluble carbon (HWSC), a decreasing trend was noticed. While the highest value of WSC and HWSC were recorded in FYM 10 t ha^{-1}, all other C fractions were higher in the treatments *viz.* soil test based POP + biochar 10 t ha^{-1} and biochar 10 t ha^{-1}. With an increase in levels of biochar, the

labile C fractions *viz.* POXC and MBC increased. The labile C fractions in soil were in the order POXC > HWSC > MBC = WSC.

As regards the N fractions, NH_4-N declined steadily at 3 months, then increased up to 9 months of incubation after which it decreased till the incubation ended. The NO_3-N and amino acid N increased up to 12 months of incubation and slightly declined thereafter. Increase in total hydrolysable N was noticed up to 6 months of incubation and thereafter, a progressive decrease was noticed. While the total N content decreased over the incubation period, the $KMnO_4$-N increased. With an increase in levels of biochar, the NO_3-N and $KMnO_4$-N increased. The treatments soil test based POP + biochar and soil test based POP were equally superior to other treatments with respect to N fractions.

Results of field experiments revealed the superiority of biochar 10 t ha^{-1} in increasing soil pH and NH_4OAc-K and reducing the exchangeable acidity. The treatments soil test based POP + biochar and soil test based POP were superior with respect to most of the soil properties. Application of biochar at 10 t ha^{-1}, either alone or in combination with POP improved the soil properties *viz.* OC, dehydrogenase activity, CEC, MWHC and hot water soluble B. With an increase in levels of biochar, the soil properties *viz.* pH, CEC, WHC, dehydrogenase activity, NH_4OAc-K, Ca, HCl-Zn and humic acid increased.

With respect to the growth parameters and yield of Chinese potato, application of soil test based POP + biochar and soil test based POP were comparable. The same treatment soil test based POP + biochar that faired in terms of direct effect proved good in residual effect as well, as reflected from the plant growth and yield of cowpea. Path analysis had shown that the soil properties *viz.* OC, MBC, Bray-P, NH_4OAc-K, Ca and EC directly influenced the tuber yield, reinstating the role of biochar in yield improvement. The nutrient content in plant parts and its uptake varied among treatments and corroborated the trend.

Considering the quality attributes of Chinese potato, the treatments biochar 10 t ha^{-1} and soil test based POP + biochar recorded higher CHO content. Protein content was highest in the treatments soil test based POP and soil test based POP + biochar. The advantage of biochar on increasing protein content and decreasing crude fibre content was visible in the succeeding crop of cowpea also, thus establishing its high residual effect.

The study revealed the potential of biochar as an amendment in the highly weathered, nutrient-poor acidic laterite soils of the tropics. Its application brought about increase in soil pH, addition of basic cations, improvement in CEC and WHC, and gradual release of nutrients to the growing plants. The overall improvement in physical, chemical and biological soil conditions through biochar could promote plant growth, yield as well as quality. The positive effect of biochar could be observed in combination with soil test based fertilizer application also.